CHAPTER 1

CHEMICAL BONDING AND INTERMOLECULAR FORCES

Atoms of elements are rarely found by themselves in nature. Everything around us is made up of elements, molecules, or compounds. The millions of different chemical compounds that make up everything on Earth are composed of 118 elements that join together in different ways. The 118 known elements interact with one another to create new, unique compounds that have entirely different chemical and physical properties from the elements that make them up. This is because the forces of attraction between the same or different atoms of these elements form molecules or compounds. The attractive forces that hold atoms together in compounds are also known as chemical bonds. All the inorganic and organic materials we use are created with the help of chemical bonding. Every day, the water we drink, the oxygen we breathe, the salt and sugar we use, the proteins we need, the carbohydrates we eat, the fuels, the gas and plastics we use, and the medicines we need to cure ourselves are all the results of chemical bonding between atoms. Chemical bonds also play an important role in all living things because they hold together the cells in our bodies. Basic concepts of bond formation, such as ionic bonds and covalent bonds between atoms and their physical properties, have been introduced in Grade 10 Chemistry. This chapter further explores different types of bonding, emphasising their strengths and structures. In addition, how to depict molecular structures of molecules and how to predict the shapes of molecules are also included.

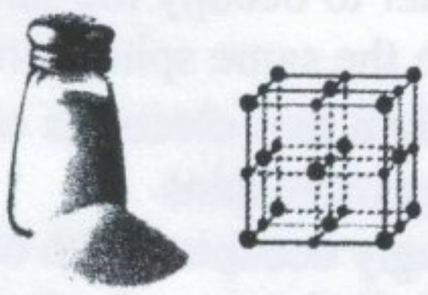
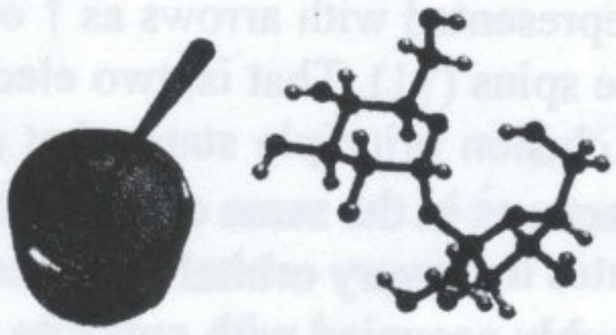
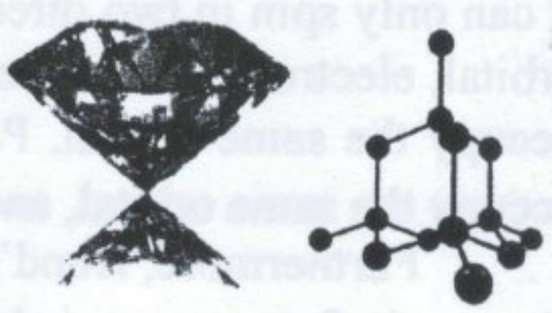


Table salt



Sugar



Diamond

Learning Outcomes

After completing this chapter, students will be able to

- indicate some basic concepts to understand chemical bonding;
- classify the types of chemical bonding;
- describe the formation of ionic bonds and ionic compounds, and the structures of ionic compounds;
- describe the formation of covalent bonds and Lewis structures of covalent molecules;
- predict the shape of covalent molecules using Valence Shell Electron Pair Repulsion (VSEPR) theory;
- distinguish between the polar and non-polar molecules;
- describe the intermolecular forces such as van der Waals forces and hydrogen bonding;
- explain the strength of metals based on metallic bonding.

1.1 BASIC CONCEPTS TO UNDERSTAND CHEMICAL BONDING

Since the discovery of the electronic structure of atoms (refer to the Grade 10 Chemistry Textbook), scientists have been able to investigate the ways in which atoms of the same or different elements can combine with one another. The outermost shell electrons **(valence electrons)** of those atoms are the basis for understanding the joining of atoms. This interaction of electrons leads to the forces of attraction, chemical bonds, that hold atoms together in substances.

Electronic structure and energy levels of electrons

In order to explain the electronic structures of atoms, the principles of filling electrons in the atomic orbitals, such as the **Aufbau principle**, **Pauli's exclusion principle**, and **Hund's rule** are fundamental to understand.

In atoms, there are K, L, M, N,... main shells and each main shell can be divided into *s*, *p*, *d*, and *f* subshells. Each subshell can be filled with 2, 6, 10, and 14 electrons, respectively. Each of these subshells contains spaces for electrons called orbitals. In addition, *s* subshell has only one spherical-shaped orbital. There are three dumbbell-shaped *p* orbitals (p_x, p_y, p_z) and the five *d* orbitals have double dumbbell-shapes.

According to the Aufbau principle (Aufbau means building up in German), **electrons are filled in the lower energy atomic orbitals before filling higher energy ones**. The order of filling the orbitals is given as 1*s* 2*s* 2*p* 3*s* 3*p* 4*s* 3*d* 4*p*.....

Moreover, to understand how many electrons can fit into an orbital, one of the properties of the electron, known as spin, has to be considered. Each electron spins on an axis, like a globe. It can only spin in two directions, represented with arrows as ↑ or ↓. In order to occupy the same orbital, electrons must have opposite spins (↑↓). That is, two electrons with the same spin cannot occupy the same orbital. Pauli's exclusion principle states that **no more than two electrons can occupy the same orbital, and two electrons in the same orbital must have opposite spins**.

Furthermore, Hund's rule states that **every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied with opposite spins, and all electrons in singly occupied orbitals have the same spin**.

On the basis of these principles and rule, the description of electronic configurations of some elements is illustrated in Figure 1.1.

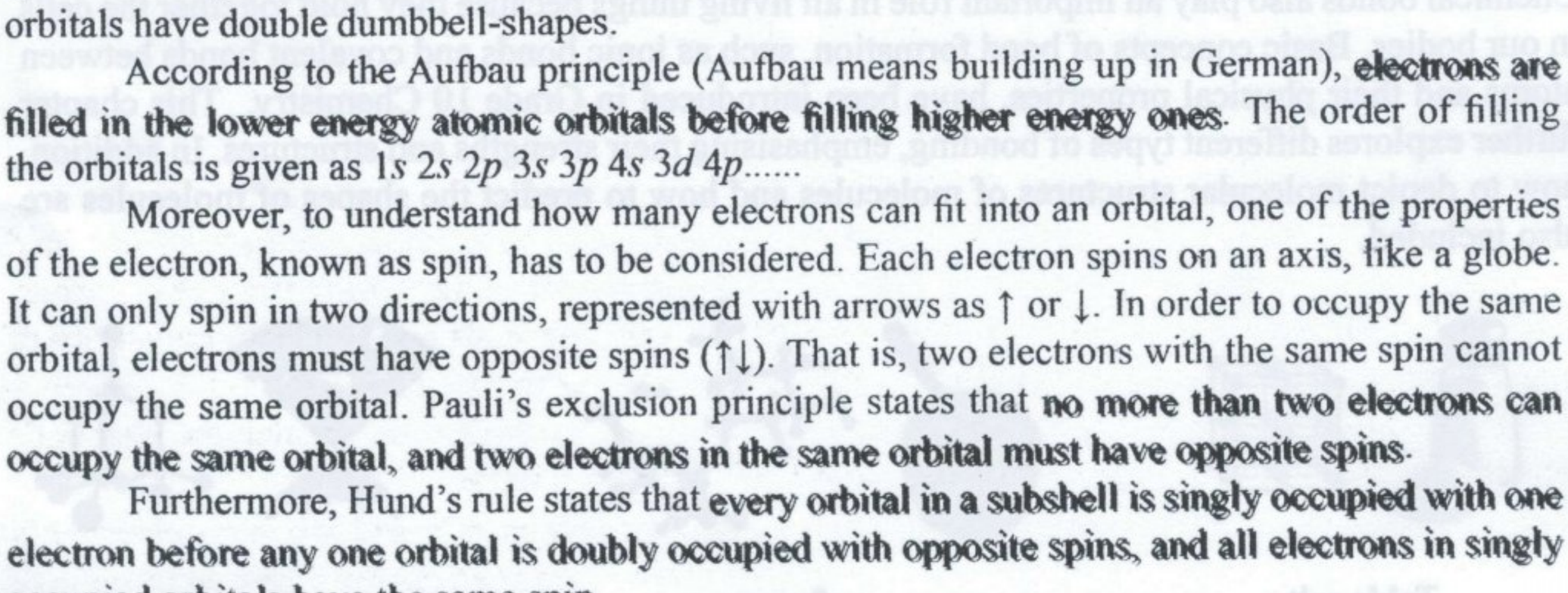


Figure 1.1 Description of Electronic Configurations of Some Elements

Valence electrons and Octet rule

The electrons in the valence shells (outermost shells) of an atom are known as the valence electrons. For an atom, the number of valence electrons is equal to its group number in the Periodic Table. For example, carbon is in Group IV and has 4 valence electrons. Oxygen is in Group VI and has 6 valence electrons.

Only valence electrons can take part in chemical bonding. **Whenever a chemical bond forms, atoms lose, gain, or share electrons in order to achieve the stable electronic structures of noble gases, i.e., eight electrons in the valence shell, which is known as the octet rule**. However, there are a few exceptions found with elements of the second period of the Periodic Table when there are an odd number of valence electrons, too few valence electrons, or too many valence electrons. Additionally, the octet rule does not apply to *d*-block elements.

To explain the chemical bonding and structures of atoms, molecules, and ions, the chemically important valence electrons occupied in *s* and *p* orbitals are represented using Lewis symbols introduced by Gilbert Newton Lewis (1875–1946), an American physical chemist. The Lewis symbols for some elements from the second period of the Periodic Table are given below. The dots represent electrons.

Electronegativity, Electron affinity and Ionisation energy

Chemical bonding is any of the interactions that allow for the association of atoms into molecules, ions, and compounds. Therefore, a chemical bond is formed when atoms are held together by the attractive forces between them after sharing or transferring the valence electrons. The strength of sharing or transferring the valence electrons depends on the electronegativity of the atoms involved in the chemical bonding. Since electronegativity (EN) is **a measure of the ability of an atom to attract the shared electrons to itself**, the greater an element's electronegativity, the stronger its attractive power to electrons will be.

In general, electron affinity (EA) is **the amount of energy released when an electron is added to a gaseous atom**, and ionisation energy (IE) is **the amount of energy required to remove an electron from a gaseous atom**. Therefore, the elements having high electron affinity easily gain electrons, resulting in the formation of the anions, and the elements having low ionisation energy easily lose electrons, resulting in the formation of the cations.

Generally, the higher the first ionisation energy of an element, the greater is its electronegativity. The higher the value of the electronegativity, the greater is the atom's attraction to electrons.

Types of chemical bonding

The type of chemical bonding depends on the types of elements (metals or non-metals) that are involved. There are three main types of chemical bonding, such as ionic bonding, covalent bonding, and metallic bonding. Although the atoms within molecules are kept together by strong forces, the forces between molecules are weak. These weak forces, called intermolecular forces, are hydrogen bonding and van der Waals forces such as ion-dipole interaction, dipole-dipole interaction, and London dispersion forces.

The types of chemical bonding and intermolecular forces are important because they can

affect the structures and physical properties of elements and compounds. In general, an ionic bond is stronger than a covalent bond. The hydrogen bond is the strongest intermolecular force followed by van der Waals forces. Among van der Waals forces, London dispersion forces are the weakest intermolecular forces that can be found in all substances.

Before we consider the details of ionic and covalent bond models, it is important to emphasise that most bonds are not 100 % ionic or 100 % covalent. Instead, most bonds have at least some degree of both ionic and covalent character.

REVIEW QUESTIONS

(1) (a) What are the lowest energy main shell and subshell that electrons occupy?
(b) What are the directions of the electron spins in the same orbital of an atom?
(c) How many orbitals are there in the *s*, *p*, and *d* subshells? What are the shapes of these orbitals?

(2) Some elements such as $_{13}Al$, $_{15}P$, $_{16}S$, $_{19}K$, $_{35}Br$, and $_{36}Kr$ are given.
(i) Describe the electronic configuration for each element.
(ii) Describe the valence electrons of the elements listed.
(iii) Give a Lewis symbol for each element.

(3) (a) What is meant by the term electronegativity of an element?
(b) What does the type of chemical bonding depend on?
(c) (i) Classify the main type of chemical bonding. Among them, which force is the strongest?
(ii) Mention the intermolecular forces.

Key Terms

- **Valence electrons** are the electrons in the outermost shell of an atom.
- **Aufbau principle** states that electrons are filled in the lower energy atomic orbitals before filling higher energy ones.
- **Pauli's exclusion principle** states that no more than two electrons can occupy the same orbital, and two electrons in the same orbital must have opposite spins.
- **Hund's rule** states that every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.

1.2 IONIC BONDING

Ionic bonding (electrovalent bonding) results from the transfer of electrons from one atom having small ionisation energy to another atom having a large electron affinity, and the **electrostatic attractions** between cations (positively charged ions) and anions (negatively charged ions) are formed.

(a) Formation of Ionic Bond

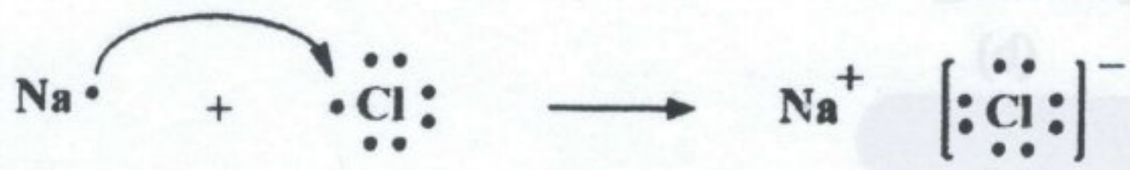
Nature of ionic bonding

Ionic bonding depends on the difference in electronegativity between two atoms. Mostly it takes place when the difference in electronegativity is greater than 1.8. It generally occurs between reactive metals and reactive non-metals. When an ionic bond forms, a metal loses electrons to form positively charged ions (cations), whereas the non-metal atom readily gains electrons to form negatively charged ions (anions). The two or more oppositely charged ions are

then attracted to each other by strong electrostatic force, which is known as an ionic bond. The number of lost or gained electrons by an atom during ionic bonding is the same as the valency of that element.

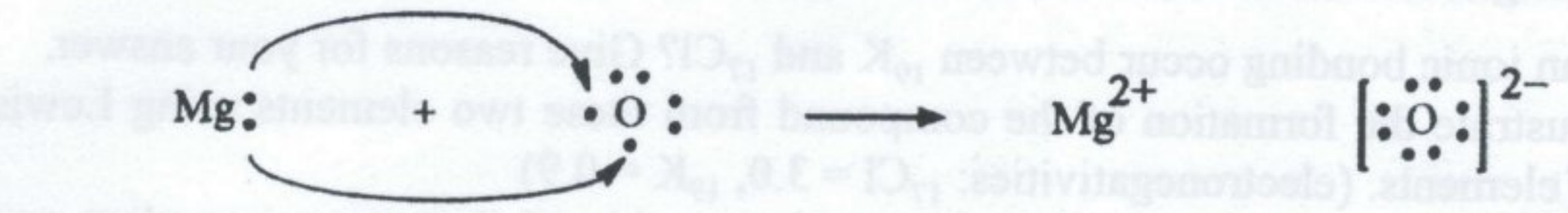
For example, in the formation of sodium chloride, one electron from a sodium atom is transferred to one chlorine atom to form a sodium ion, Na^+ and a chloride ion, Cl^- because the difference in electronegativity between Na (0.9) and Cl (3.0) is 2.1. As a result, both ions, Na^+ and Cl^-, have the electronic configurations of noble gases Ne and Ar, respectively. They differ, however, from neutral atoms of Ne and Ar by carrying their respective ionic charges. The electrostatic attraction resulting from the opposite charges constitutes ionic bonds. The ions arrange themselves into a crystal lattice. Since electrons loss always equals electrons gain in an electron transfer process, **ionic compounds** are always neutral. The ratio in which positive and negative ions combine is the ratio that achieves neutrality of the resulting compound. The Na^+ and Cl^- ions can be present only in a 1:1 ratio in the sodium chloride compound, so the formula must be NaCl.

By using Lewis symbols of Na and Cl, the Lewis structure of NaCl can be illustrated as below.



sodium chloride, NaCl

In the case of magnesium oxide (MgO), since the electronegativity difference (2.3) between Mg (1.2) and oxygen (3.5) is greater than 1.8, Mg loses two electrons, and oxygen gains two electrons. It results in Mg^{2+} and O^{2-} ions with the electronic configuration of stable noble gas (Ne). The formation of MgO can be described using Lewis symbols of the elements as below.



magnesium oxide, MgO

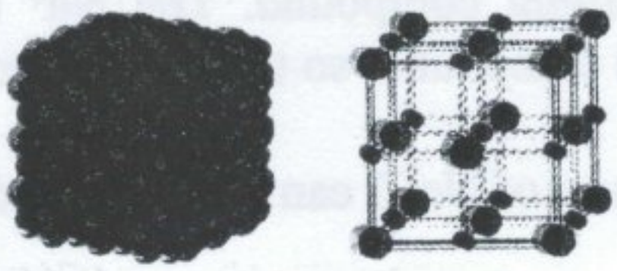
(b) Structures of Ionic Compounds

In ionic compounds, the cations and anions are held together by strong electrostatic attraction. In general, the greater the charge on the ions, the greater the electrostatic attraction and the stronger the ionic bond will be. So, the melting points of the ionic compounds with the greater charge on the ions are higher. In solid ionic compounds, their ions are held in fixed positions and cannot move, and hence they cannot conduct electricity.

In the crystalline state of ionic compounds, the oppositely charged ions are held together in orderly three-dimensional arrangements, forming giant

structures. The crystalline structure of an ionic solid is called a **crystal lattice**, created by repeating **unit cells**. The unit cells can be of different types, such as cubic unit cells. The cubic unit cell can have three types: **simple cubic (sc) unit cell, face-centred cubic (fcc) unit cell**, and **body-centred cubic (bcc) unit cell**, as shown in the illustrations.

For example, sodium chloride (rock salt, NaCl), a white crystalline solid, does not contain one Na^+ ion and one Cl^- ion, but a lot of these two ions are arranged in a crystal lattice (Figure 1.2). It has a cubic structure and is formed by repeating the face-centred cubic (fcc) unit cell. So, each Na^+ ion has six neighbouring Cl^- ions, and each Cl^- ion has six neighbouring Na^+ ions. The term **coordination number** is used to express the number of ions surrounding the central ion in the lattice. Since the coordination ratio of Na^+ ion to Cl^- ion is 6:6, the simple ratio of 1:1 gives the formula unit of sodium chloride which is NaCl.



● Na^+ ion
● Cl^- ion

Figure 1.2 (a) NaCl Crystal and (b) Crystal Lattice Arrangement in Its Unit Cell

REVIEW QUESTIONS

(1) (a) What is the result of the transfer of electrons from one atom to another atom?
(b) What are the necessary conditions to form an ionic compound between two atoms?
(c) Which of the following pairs can form an ionic compound?
Give reasons for your answers.
(i) H and O (ii) Li and O (iii) C and O (iv) Ca and O

(2) Compare two given ionic compounds: NaCl and $CaCl_2$, in terms of (i) electrostatic attraction, (ii) strength of ionic bond, and (iii) melting point.

(3) (a) Can ionic bonding occur between $_{19}K$ and $_{17}Cl$? Give reasons for your answer. Illustrate the formation of the compound from these two elements using Lewis symbols of elements. (electronegativities: $_{17}Cl = 3.0$, $_{19}K = 0.9$)
(b) In a sodium chloride crystal lattice, how many chloride ions are surrounding a sodium ion in a unit cell? What are the coordination ratio and formula of sodium chloride?

Key Terms

- **Electrostatic attraction** is the attraction between a negatively charged ion and a positively charged ion.
- **Ionic compounds** are compounds that consist of ions and predominantly contain ionic bonding.
- **Crystal lattice** is a geometric arrangement of the points in space at which the atoms, molecules, or ions of a substance occur.
- **Unit cell** is the smallest repeating unit of a crystal lattice that shows the three-dimensional pattern of the entire crystal.
- **Simple cubic unit cell** is a cubic cell with an atom in each corner of the cube.
- **Face-centred cubic unit cell** is a cubic cell with an atom on each corner, and an atom at the centre of each face.

- **Body-centred cubic unit cell** is a cubic cell with an atom on each corner and another in the centre of the cube.
- **Coordination number** is the number of atoms or ions surrounding a central atom in a crystal lattice.

1.3 COVALENT BONDING

Covalent bonding can occur between similar or even identical atoms. The concept of electron sharing rather than electron transfer explains bonding between similar or identical atoms. As a result, a covalent bond is formed by sharing one or more pairs of valence electrons between atoms. Thus, the covalent bond is the electrostatic attraction between the nuclei of the atoms and the shared electrons. Covalent bonding usually occurs between non-metals. Many inorganic substances and millions of organic compounds have covalent bonding.

(a) Formation of Covalent Bonds

Consider the formation of a covalent bond between two hydrogen atoms to form a diatomic molecule (H_2) as an example. If two hydrogen atoms are approaching one another, three forces act on the atoms at the same time (Figure 1.3).

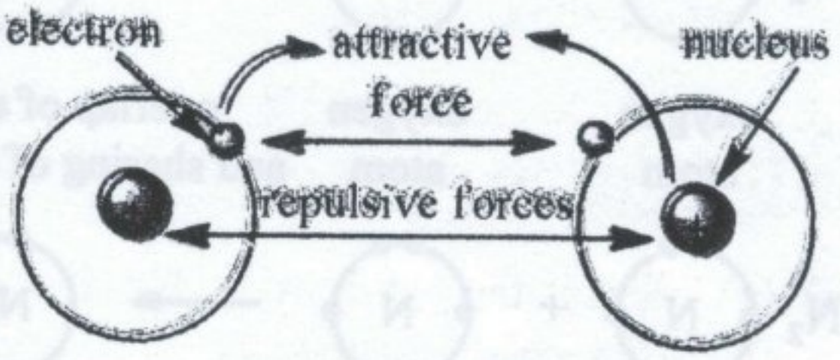


Figure 1.3 Forces Acting on Two Approaching Hydrogen Atoms

These three forces are (1) repulsive force between the electrons of atoms since like charges repel, (2) attractive force between the nucleus of each atom and the electrons of another, and (3) repulsive force between the two positively charged nuclei. The magnitudes of the attractive and repulsive forces between nuclei and electrons depend on the distance between the atoms.

For instance, when the hydrogen atoms are isolated, the attractive forces are small, and no bond is formed. When the hydrogen atoms are too close to each other, the repulsive interaction between two nuclei becomes so strong that it pushes them apart. Consequently, there is an optimum distance between two nuclei called the bond length where net attractive forces are maximised and the most stable covalent bond is formed in the H-H molecule.

Nature of covalent bonding

In covalent bonding, the outermost orbitals of the atoms overlap so that ***unpaired valence electrons*** in each of the bonding atoms can be shared, whereas the ***paired valence electrons*** are not involved in bonding. By overlapping orbitals, the outer shells of all the bonding atoms are filled with valence electrons by following the octet rule. This results in an attraction between the negatively charged electrons and the positively charged nuclei, and this force holds the atoms together in a covalent bond. The covalent bonding formed in some simple molecules (HF, O_2, and N_2) is shown in Figure 1.4 as examples.

The covalent bonds can be single bonds or multiple covalent bonds, namely double bonds (e.g., O_2, CO_2, C_2H_4, etc.) and triple bonds (e.g., N_2, CO, etc.). In single covalent bonds, only one pair of electrons is shared between two atoms. A double bond is formed by sharing two pairs of electrons between two atoms, whereas a triple bond is formed by sharing three pairs of electrons.

The length of the bond is determined by the number of bonded electrons. The higher the number of bonded electrons, the stronger the attraction between the two atoms and the shorter the bond length.

So, the bond length of the single bond is the longest, followed by the double bond and triple bond. In contrast, the bond strength of the triple bond is the highest, followed by the double bond and single bond.

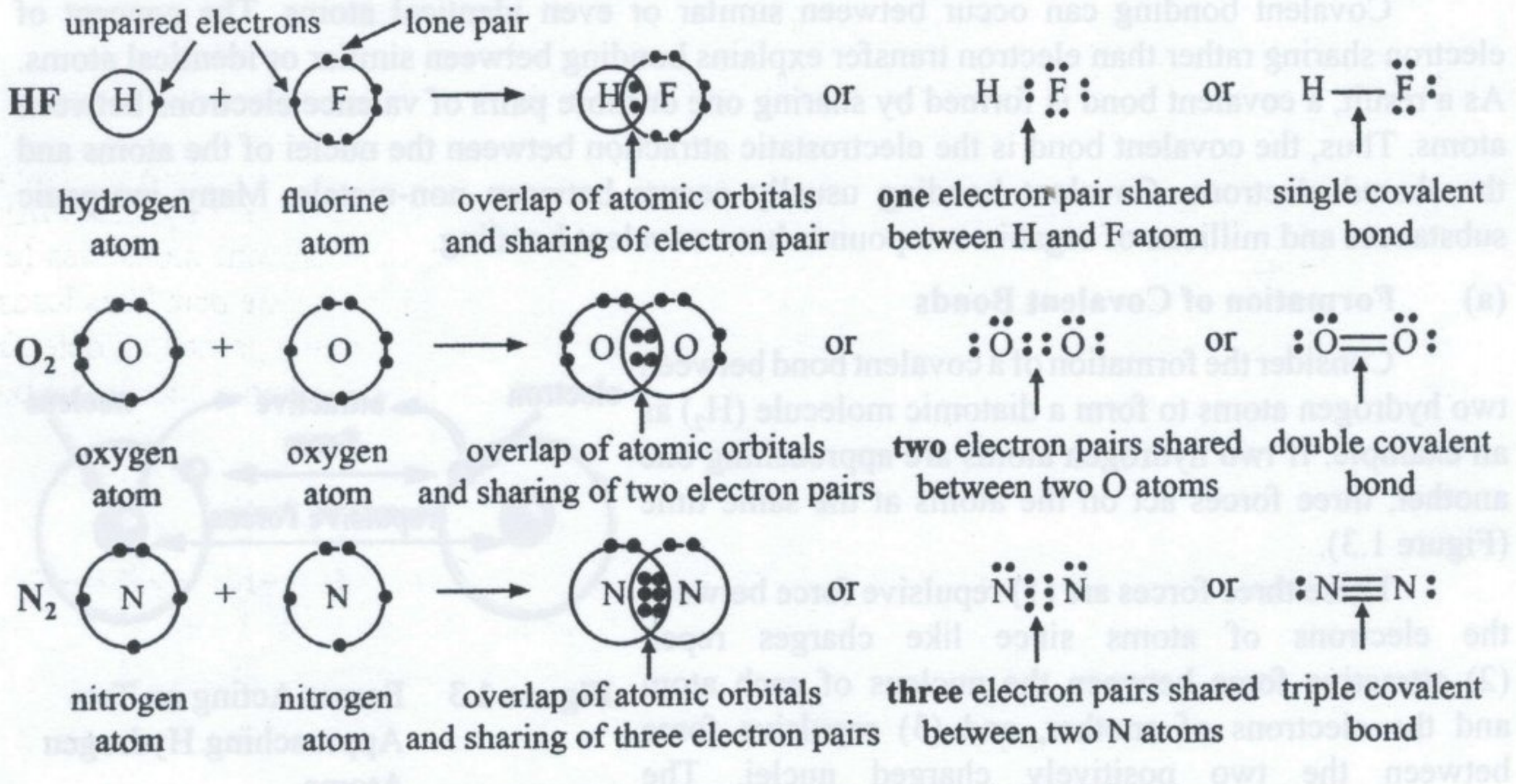
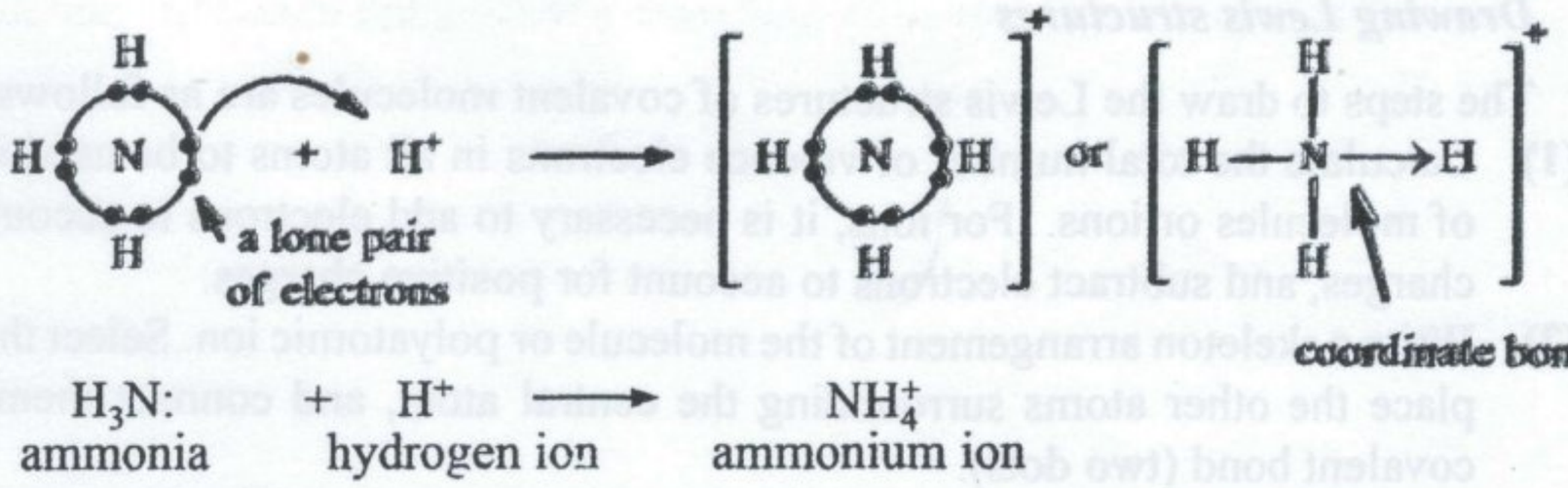


Figure 1.4 Covalent Bonding in HF, O_2, and N_2 Molecules

Formation of coordinate bonds (Dative bonds)

A **coordinate bond**, or dative bond, is a special type of covalent bond. This bond is characterised by the fact that the two shared electrons are both donated by one of the participating atoms. This is quite different from an ordinary covalent bond, where the two bonded atoms each contribute an electron towards the formation of the bond. A coordinate bond is formed when one of the participating atoms possesses an unshared pair (a lone pair) of electrons. This lone pair is donated to an atom needing them to build up, or complete, a stable electron octet or duplet. A coordinate bond is expressed as an arrow, $\longrightarrow$ which indicates the direction in which the electrons are donated.

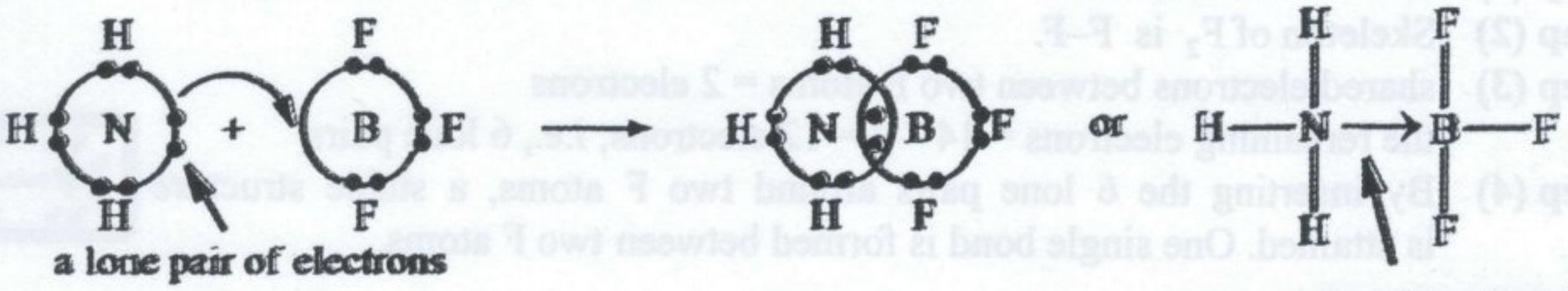
The formation of NH_4^+ or H_3O^+ ions is an example of the formation of a coordinate bond. The ammonia molecule possesses a lone pair of electrons on the nitrogen atom; it can be donated to a hydrogen ion to produce the ammonium ion NH_4^+, forming a coordinate bond. This bonding produces an electron duplet to the hydrogen nucleus while the stable electron octet structure of the nitrogen atom in ammonia still remains. As a result of the combination, the positive charge on the hydrogen ion is carried over to give the positively charged ammonium ion, NH_4^+ (Figure 1.5). The arrow $\longrightarrow$ indicates the source of both electrons which constitute the bond. Note that the nitrogen is bonded to four identical atoms of the same element (H); and all four single bonds, once they have been formed, are identical.



H_3N: + H^+ ⟶ NH_4^+
ammonia hydrogen ion ammonium ion

Figure 1.5 Formation of a Coordinate Bond in the Ammonium Ion

Similarly, a water (H_2O) molecule that possesses two lone pair electrons on the oxygen atom can react with a hydrogen ion, H^+, through a coordinate bond, giving a hydronium ion, H_3O^+. In addition, molecules with incomplete octets, called electron-deficient molecules (e.g., $BeCl_2$, BF_3, $AlCl_3$), can accept an electron pair from a molecule bearing a lone pair. This leads to the formation of a coordinate compound in which the central atom has now gained an octet. For example, an ammonia molecule can combine with boron trifluoride, BF_3 using a coordinate bond to form the $H_3N \rightarrow BF_3$ molecule, as illustrated in Figure 1.6.



H_3N: + BF_3 ⟶ $H_3N \rightarrow BF_3$
ammonia boron trifluoride adduct

Figure 1.6 Formation of a Coordinate Bond between NH_3 and BF_3

In carbon monoxide, the CO molecule has a triple bond that consists of two covalent bonds and one coordinate bond where both electrons come from the O atom. Figure 1.7 shows the chemical bonding in the CO molecule, C≡O.

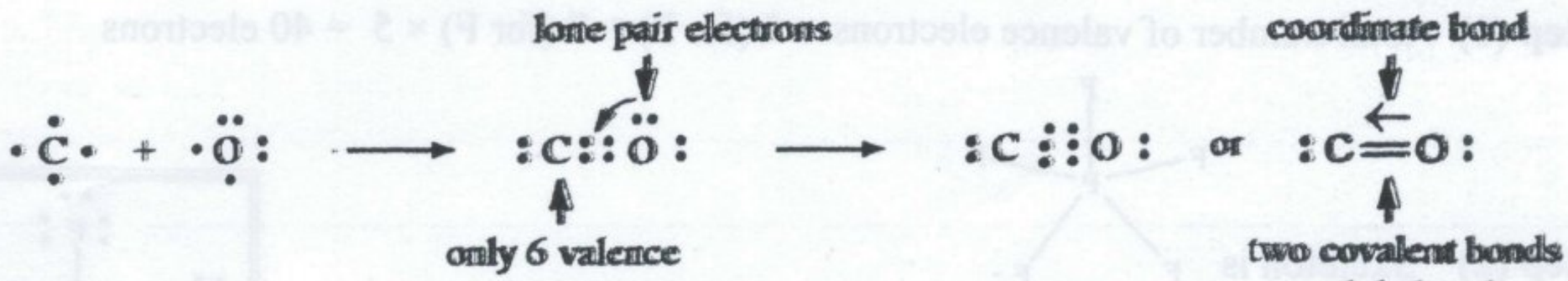


Figure 1.7 Chemical Bonding in Carbon Monoxide Molecule

(b) Lewis Structures of Molecules and Polyatomic Ions

Lewis structures are only two-dimensional representations of how the valence shell electrons are arranged around individual atoms in a molecule or an ion. In a Lewis structure, a covalent bond is described by writing each shared electron pair either as a pair of two dots between symbols of two atoms or as a line connecting them.

Drawing Lewis structures

The steps to draw the Lewis structures of covalent molecules are as follows:

Step (1) Calculate the total number of valence electrons in all atoms to be used in the structure of molecules or ions. For ions, it is necessary to add electrons to account for negative charges, and subtract electrons to account for positive charges.

Step (2) Write a skeleton arrangement of the molecule or polyatomic ion. Select the central atom, place the other atoms surrounding the central atom, and connect them with a single covalent bond (two dots).

Step (3) Subtract the number of electrons used in shared pairs from the total number of valence electrons. Place the remaining electrons into the skeleton as unshared pairs. Use double and triple bonds only if necessary.

Step (4) Insert the unshared paired electrons (lone pairs) into the skeleton to complete the octet of every element (except H, which can share only 2 electrons).

Some examples are given below.

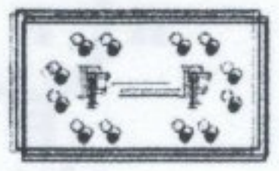
For $\mathbf{F_2}$ molecule,

Step (1) the total number of valence electrons = 7 valence electrons (for F) × 2 = 14 electrons

Step (2) Skeleton of F_2 is F–F.

Step (3) shared electrons between two F atoms = 2 electrons
the remaining electrons = 14 – 2 = 12 electrons, i.e., 6 lone pairs

Step (4) By inserting the 6 lone pairs around two F atoms, a stable structure is attained. One single bond is formed between two F atoms.



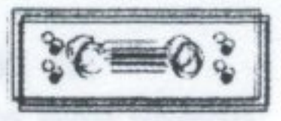
For **CO** molecule,

Step (1) the total number of valence electrons = 4 (for C) + 6 (for O) = 10 electrons

Step (2) Skeleton of CO is C–O.

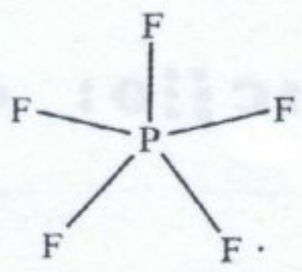
Step (3) shared electrons between C and O atoms = 2 electrons
the remaining unshared electrons = 10 – 2 = 8 electrons, i.e., 4 lone pairs

Step (4) The 4 lone pairs are placed around C and O atoms to attain stable structure. So, the CO molecule contains a triple bond between C and O atoms.



For $\mathbf{PF_5}$ molecule,

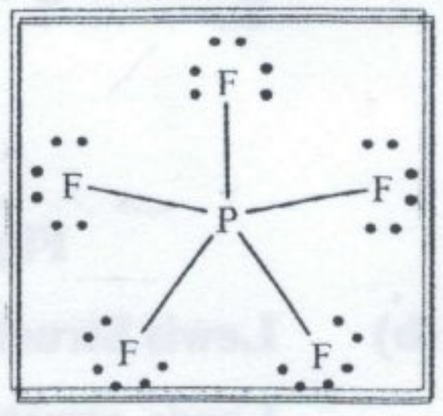
Step (1) total number of valence electrons = 5 (for P) + 7 (for F) × 5 = 40 electrons



Step (2) Skeleton is .

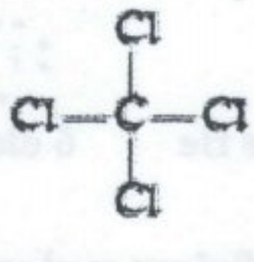
Step (3) shared electrons = 10 electrons
the remaining electrons = 40 – 10 = 30 electrons, i.e., 15 lone pairs

Step (4) The 15 lone pairs are placed around five F atoms to get a stable structure. So, five single bonds are present in PF_5.

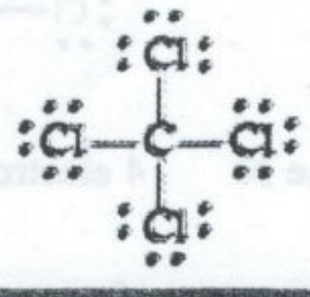


Example 1: Draw the Lewis structure of carbon tetrachloride, CCl_4 molecule.

Solution: total number of valence electrons = 4 (for C) + 7 (for Cl) × 4 = 32 electrons
shared electrons = 8 electrons
the remaining electrons = 32 – 8 = 24 electrons, i.e., 12 lone pairs



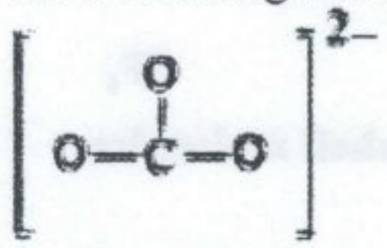
skeleton



Lewis structure of CCl_4
4 single bonds

Example 2: Draw the Lewis structure for the carbonate ion, CO_3^{2-}.

Solution: total number of valence electrons = 4 (for C) + 6 (for O) × 3 + 2 electrons
(from 2 negative charges)
= 24 electrons
shared electrons = 6 electrons
the remaining unshared electrons = 24 – 6 = 18 electrons, i.e., 9 lone pairs



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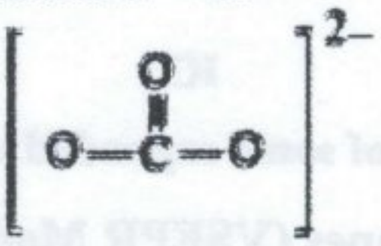
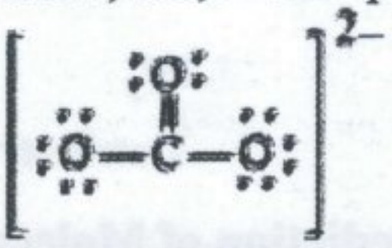


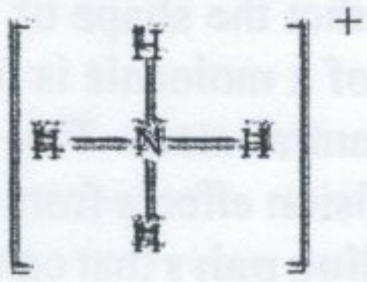
Place 2 electrons at the C atom to attain stable structure.



Lewis structure of CO_3^{2-}
2 single bonds and one double bond

Example 3: Draw the Lewis structure for the ammonium ion, NH_4^+.

Solution: total number of valence electrons = 5 (for N) + 1 (for H) × 4 – 1 electron
(for one positive charge)
= 8 electrons
shared electrons = 8 electrons
the remaining unshared electrons = 8 – 8 = 0 electron, i.e., no lone pair



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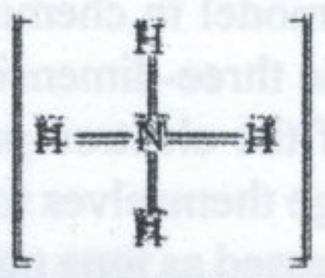
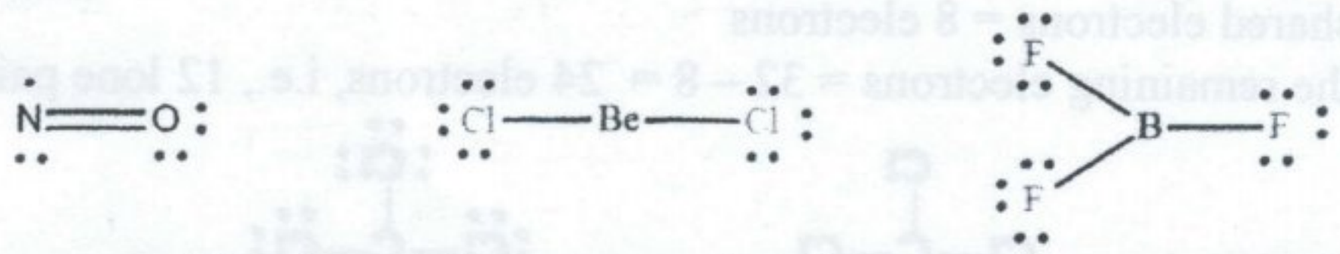


Lewis structure of NH_4^+
4 single bonds

Exceptions to the octet rule

Some molecules that deviate from the octet rule, such as **electron-deficient molecules** (e.g., NO, $BeCl_2$, BF_3, BCl_3, $AlCl_3$) and **expanded valence shell molecules** (e.g., PF_5, ICl_3, SF_6) can occur. The central atom in an electron-deficient molecule has valence electrons of less than 8, and that in an expanded valence shell molecule has valence electrons of more than 8.

The Lewis structures of some molecules that deviate from the octet rule are illustrated in the following figures:

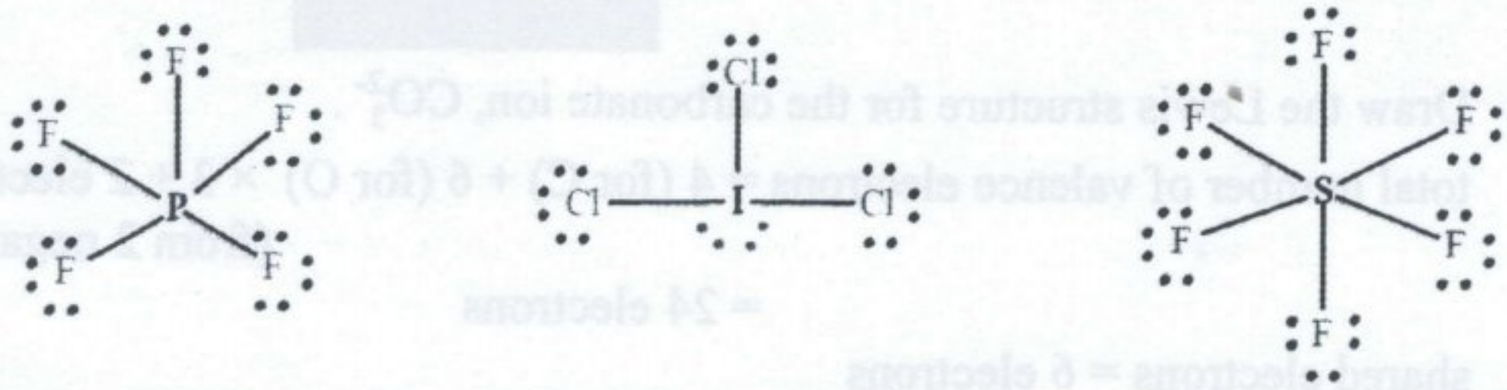


7 electrons around the N — NO

4 electrons around the Be — $BeCl_2$

6 electrons around the B — BF_3

Lewis structures of some electron-deficient molecules



10 electrons around the P — PF_5

10 electrons around the I — ICl_3

12 electrons around the S — SF_6

Lewis structures of some expanded valence shell molecules

(c) Prediction of Molecular Shapes (VSEPR Model)

The Lewis structures provide a simple way to predict the distribution of valence electrons and bond lengths in a molecule. Covalent molecules take on definite shapes that depend upon the number of bonds involved and the number of unshared electron pairs around an atom. The molecular shape in which the atoms and electron pairs exist in a three-dimensional arrangement can be predicted by using the **Valence Shell Electron Pair Repulsion (VSEPR - pronounce vesper) theory**. In modern days, the description of the electronic structure of a molecule can be explained using the **molecular orbital theory (MOT)**.

Valence shell electron pair repulsion (VSEPR) theory

This theory is a model in chemistry used to predict the shape of covalent molecules. It is based on the idea that the three-dimensional geometry of a molecule is mostly determined by the repulsive interactions of the electron pairs around a central atom. This model assumes that the electron pairs will arrange themselves to minimise repulsion effects from one another. These pairs of electrons may be expressed as **lone pairs** and/or **bonding pairs** that can influence the **molecular shape**. In the case of molecules containing multiple bonds (i.e., double bonds and triple bonds), these bonding pairs behave as a single unit.

The repulsive interaction of electron pairs increases in the order of -

bonding pair-bonding pair < lone pair-bonding pair < lone pair-lone pair.

The lone pairs are localised on the central atom while each bonding pair is shared between two atoms. These lone pairs of electrons in a molecule occupy more space compared with the bonding pairs of electrons. Thus, the repulsion between lone pairs of electrons is greater as compared to the lone pair-bonding pair and bonding pair-bonding pair repulsions. These repulsion effects result in deviations from the idealised shapes and alternations in **bond angles** in molecules.

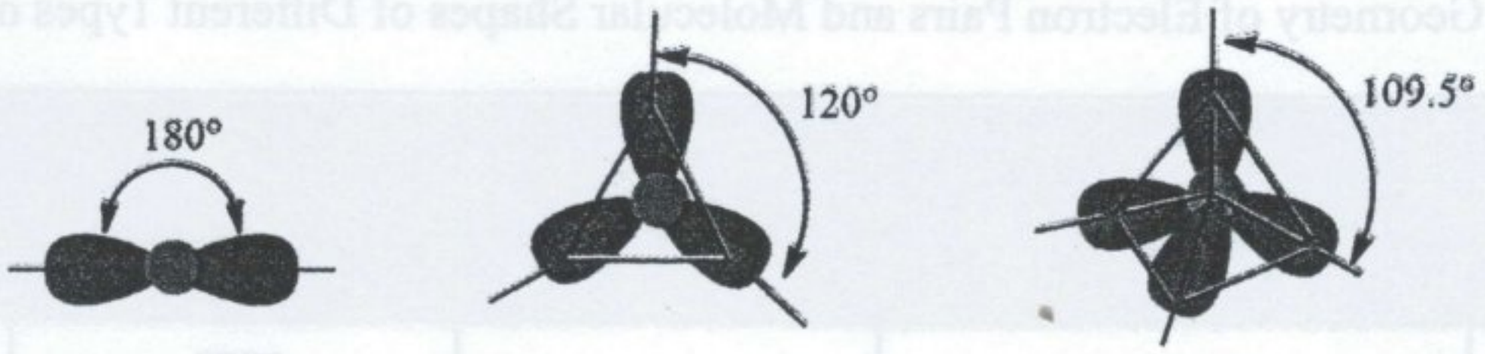
Prediction of the shape of a covalent molecule

To predict the shape of a molecule, the steps to be followed are shown below.

Step (1) Draw the Lewis structure of the molecule.

Step (2) Count the number of electron pairs around the central atom.

Step (3) Determine the geometry of electron pairs as linear or triangular planar or tetrahedral.



linear **triangular planar** **tetrahedral**

Geometry of electron pairs around the central atom

Step (4) Predict the shape of molecule.

All diatomic molecules represent two points in space and are joined by a straight line, i.e., they are linear, e.g., H_2, O_2, N_2, F_2, Cl_2, Br_2, I_2, and CO. There is no central atom in these molecules.

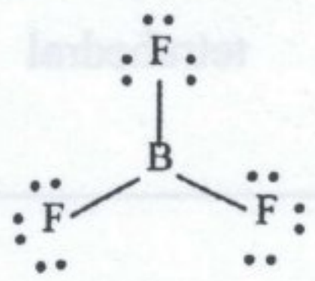
As shown in Table 1.1, a triatomic molecule (AX_2 type) has a linear shape. In this type, it has only two bonding pairs without lone pairs. For example, in $BeCl_2$, there are two bonding pairs (two single bonds) without lone pairs. Thus, the shape of $BeCl_2$ is linear. In the CO_2 molecule, there are four bonding pairs (two double bonds) without lone pairs. These four bonding pairs (two double bonds) are considered as two single units. Hence, the shape of CO_2 is linear.

Apart from AX_2 molecules, the other types of molecules which have bonding pairs without lone pairs around the central atom are similar to the geometry of the bonding pairs. If the lone pair is present in these types, the molecular shapes are not the same as the geometry of electron pairs. It is due to the electron pair repulsion between bonding pairs and lone pairs. For example, AX_3 has a triangular planar and AX_2E, where E represents a lone pair, has a V-shape (bent).

Geometry of electron pairs and molecular shapes of different types of molecules are summarised in Table 1.1.

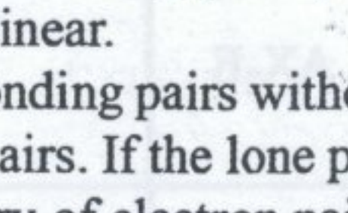
Example 4: Predict the shape of a molecule of BF_3 in terms of -
(i) Lewis structure and (ii) VSEPR model. What will be the bond angle of F-B-F?

Solution:

(i) Lewis structure of BF_3 is 

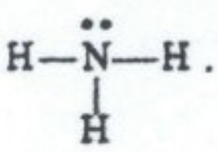
(ii) It consists of 3 electron pairs around the central atom B.
The geometry of electron pairs is triangular planar.

So, it has a triangular planar shape. The bond angle of F-B-F is 120°.

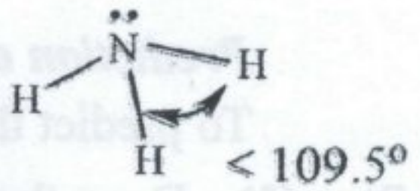


Example 5: Predict the shape of a molecule of NH_3 in terms of -
(i) Lewis structure and (ii) VSEPR model. What will be the bond angle of H-N-H?

Solution:

(i) Lewis structure of NH_3 is 

(ii) Four electron pairs are around the central atom N.



Thus, the geometry of the electron pairs is tetrahedral. There is a lone pair on the nitrogen atom. Because of the electron pair repulsion between this lone pair and the bonding pair, the shape of the molecule is trigonal pyramidal. The bond angle of H-N-H will be less than 109.5°.

Table 1.1 Geometry of Electron Pairs and Molecular Shapes of Different Types of Molecules

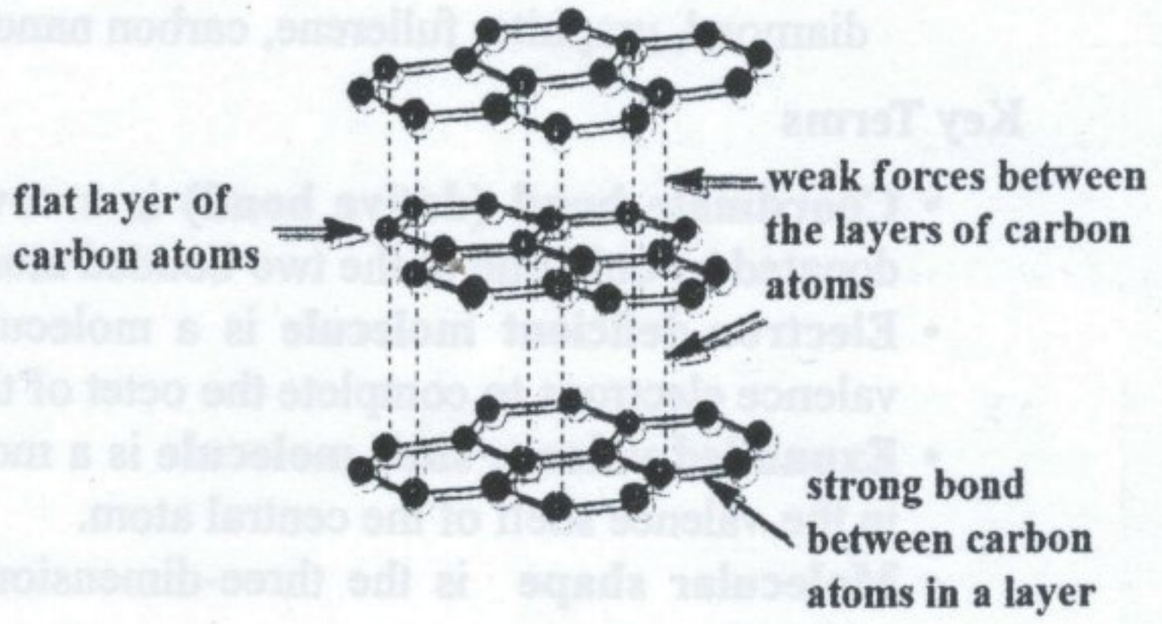
Type	Number of bonding pairs and lone pairs around the central atom	Geometry of electron pairs	Molecular shape	Example
AX_2	2, 0	linear	180° X A X linear	$BeCl_2$, CO_2
AX_3	3, 0	triangular planar (trigonal planar)	X 120° A X X triangular planar	BF_3
AX_2E	2, 1	triangular planar (trigonal planar)	A X X <120° bent/V-shaped	SO_2
AX_4	4, 0	tetrahedral	X 109.5° A X X X tetrahedral	CH_4, CCl_4
AX_3E	3, 1	tetrahedral	A X X X < 109.5° trigonal pyramidal	NH_3
AX_2E_2	2, 2	tetrahedral	A X X < 109.5° bent/V-shaped	H_2O

Note: Symbol E represents the number of lone pairs.

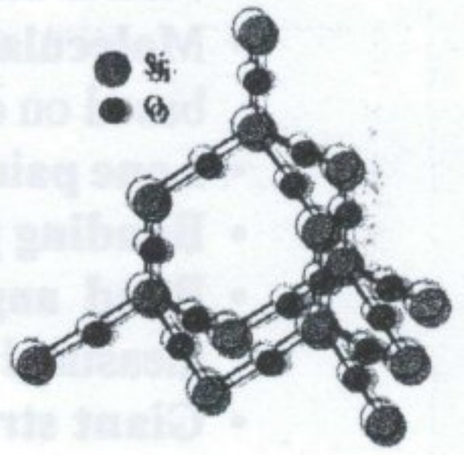
(d) Giant Structures of Covalent Molecules

Some elements occur in solids where the atoms are held together by single covalent bonds, existing as giant structures. For example, in a diamond, each carbon atom is joined to four other carbon atoms by strong covalent bonds, and the carbon atoms form a regular tetrahedral network resulting in a **giant structure**. There are no free electrons.

In the case of graphite, it has a layer and planar structure formed by joining each carbon atom to the other three carbon atoms by covalent bonds. Each layer is formed with hexagonal rings of carbon atoms. There are weak van der Waals forces between the layers, which give rise to a giant structure. In contrast to diamond, graphite has free-moving electrons in each layer. That is why graphite can conduct electricity. Although diamond and graphite are giant molecules, other synthetic allotropes of carbon, such as fullerene (C_{60}), carbon nanotubes, and graphene, do not exist as giant structures. They are only bulky covalent molecules.



Silicon(IV) oxide, SiO_2 (silica or quartz) is an example of a giant covalent molecule. In quartz, each silicon atom is bonded to four oxygen atoms, but each oxygen atom is bonded to only two silicon atoms. The oxygen atoms are formed as bridges between the tetrahedrally bonded silicon atoms. It has a similar structure to a diamond. They also have similar properties. It does not conduct electricity because it has no free moving electrons.



REVIEW QUESTIONS

(1) (a) Which of the following pairs can form covalent bonding? Give a reason for your choice.
Li and Cl B and F S and O K and O C and H

(b) Draw the Lewis structure and indicate the lone pair and bonding pair electrons in N_2 molecule.

(c) Write Lewis structures for the simplest compound formed from the following pairs of elements: (i) H and S (ii) C and Cl

(2) (a) You are given two substances: AlF_3 and $AlCl_3$. (electronegativities: F = 4.0, Al = 1.5, Cl = 3.0)
Which one is a covalent molecule? Which one is an ionic compound?

(b) Refer VSEPR theory, for the covalent molecule that you have chosen from Question 2 (a), answer in terms of -
(i) Lewis structure (ii) central atom of the molecule
(iii) number of valence electron pairs around the central atom
(iv) geometry of electron pairs (v) molecular shape

(3) (a) You are given two covalent molecules: NH_3 and BF_3.
(i) Draw their Lewis structures.
(ii) Which one has a lone pair electrons in the central atom?
(iii) Which one is an electron-deficient molecule?
(iv) Can these two molecules react? If so, write a chemical equation for it.
(v) Identify the chemical bond formed between these two molecules.
(b) Which of the following are giant covalent molecules?
diamond, graphite, fullerene, carbon nanotube, silica

Key Terms

- **Coordinate bond (dative bond)** is a covalent bond that consists of a pair of electrons donated by only one of the two bonded atoms.
- **Electron-deficient molecule** is a molecule in which there is an insufficient number of valence electrons to complete the octet of the central atom.
- **Expanded valence shell molecule** is a molecule in which there are more than 8 electrons in the valence shell of the central atom.
- **Molecular shape** is the three-dimensional arrangement of the atoms that constitute a molecule.
- **Valence Shell Electron Pair Repulsion (VSEPR) theory** is a theory used to predict the shapes of molecules and ions, based on the repulsive interactions of the electrons around a central atom.
- **Molecular orbital theory** is a method for describing the electronic structure of molecules based on quantized energy levels.
- **Lone pair** (unshared pair) is an electron pair that is not involved in bonding with other atoms.
- **Bonding pair** is an electron pair being shared by the atoms.
- **Bond angle** is an angle between any two bonds that include a common atom, usually measured in degrees.
- **Giant structure** is a three-dimensional structure of atoms that are joined by a network of bonds.

1.4 INTERMOLECULAR FORCES

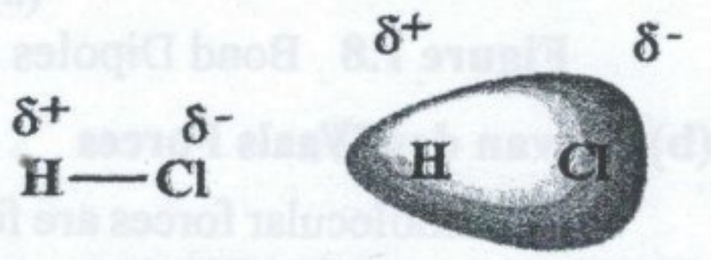
Molecules in a substance are formed by joining atoms together, and there are attractive and repulsive forces that arise between the molecules. These forces are known as **intermolecular forces**, which are responsible for most of the physical and chemical properties of matter. A covalent bond within a molecule is described as a pair of electrons shared between the atoms. If the atoms are not identical, the electrons will not be equally shared. The atom with the greater share of the electrons will be slightly negative and the other atom will be slightly positive. This is known as bond polarity. Thus, bond polarity within a molecule results in a separation of charge over the molecule. Moreover, a dipole moment of the molecule can be expressed numerically by taking into account the magnitude of the charge and the distance separating the charges. Different types of intermolecular forces can happen depending on the **polarity** of the molecules in a substance. The electronegativity of bonded atoms and the geometry of molecules play an important role in determining their polarity.

(a) Polar and Non-polar Molecules

Polar and non-polar covalent bonds

Depending on the difference in electronegativity between two bonded atoms, covalent bonds can be polar or non-polar.

If two different non-metal atoms are bonded, then the atom with the higher electronegativity will attract the shared electron pair more strongly. It results in a **polar covalent bond** being formed where one atom with higher electronegativity will have a partially negative charge (δ^-), and the other will have a partially positive charge (δ^+), known as a **dipole**. For example, since the electronegativity of Cl (3.0) is higher than that of hydrogen (2.1), the electron pair is unequally shared between Cl and H atoms. So, the covalent bond formed in HCl is polar, and it can be described as $\overset{\delta+}{H}-\overset{\delta-}{Cl}$. The δ^+ or δ^- signifies a partial positive or a partial negative charge that is less in magnitude than the charge associated with a free proton (1+) or electron (1−).



unequally sharing electrons in H-Cl

The bond becomes more polar as the difference in electronegativity values of the atoms in a covalent bond increases. For example, the H–F bond is more polar than H–Cl, H–Br, and H–I.

Difference in electronegativity: H–F > H–Cl > H–Br > H–I

Bond polarity: H–F > H–Cl > H–Br > H–I

In a covalent bond formed between two similar non-metal atoms, the shared electron pair is equally attracted to the two atoms resulting in a **non-polar covalent bond**, e.g., Cl—Cl as illustrated in the figure.

equally sharing electrons in Cl-Cl

As a result of the dipole formed in a polar covalent bond, the bond possesses the **dipole moment**. The degree of bond polarity is measured as a dipole moment of a bond.

The direction of the dipole can also be shown by the ⟷ sign. The direction of arrow points to the negative end of the dipole. For example, in the polar hydrogen chloride (HCl) molecule, hydrogen is presented as $H^{\delta+}$ and chlorine as $Cl^{\delta-}$, and it can be described as $\overset{\delta+}{H}\longrightarrow\overset{\delta-}{Cl}$. So, any individual polar covalent bond possesses a dipole moment. However, any non-polar covalent bond has a zero dipole moment, e.g., the dipole moment of Cl-Cl is zero.

Polar and non-polar molecules

Polar or non-polar molecules can be determined according to the total dipole moments of the molecules. All diatomic molecules containing polar covalent bonds are **polar molecules** since they have dipole moments.

In the case of polyatomic molecules, their dipole moments depend not only on the individual bond dipoles but also on the shape of the molecules. In such cases, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds.

For example, the H_2O molecule has a bent shape. It is a polar molecule. A net dipole moment of an H_2O molecule will occur from the total dipole moments of two O–H bonds as shown in Figure 1.8 (a).

In the case of the CO_2 molecule, it is linear and the two polar bonds are arranged

symmetrically. The two equal bond dipoles point in opposite directions and cancel the effect of each other. Thus, the dipole moment of CO_2 is zero (Figure 1.8 (b)), and it is a **non-polar molecule**.

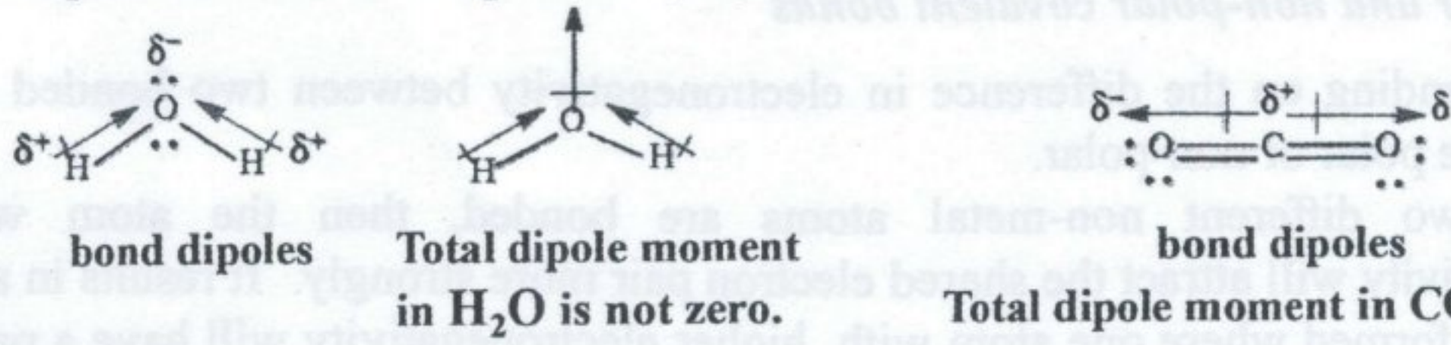


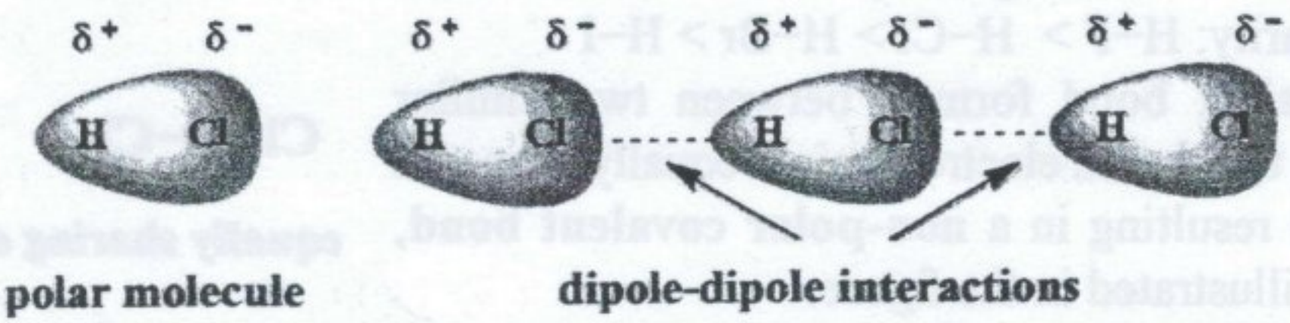
Figure 1.8 Bond Dipoles and Dipole Moments of (a) H_2O and (b) CO_2 Molecules

(b) van der Waals Forces

Intermolecular forces are forces that act between a molecule and another molecule. It can be classified as **van der Waals forces** and hydrogen bonding. Van der Waals forces are weak forces which include dipole-dipole interaction, ion-dipole interaction, and London dispersion forces.

Dipole-dipole interaction

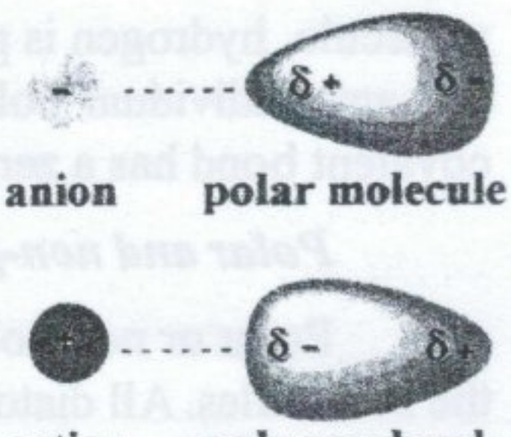
Dipole-dipole interactions are formed when two dipolar molecules interact with each other in space. When this occurs, the partially negative portion of one of the polar molecules is attracted to the partially positive portion of the second polar molecule as shown in the following figure:



For example, polar molecules such as HCl, HCN, SO_2, etc., are held together by dipole-dipole interactions.

Ion-dipole interaction

This type of intermolecular force is formed from the interaction between an ion and a dipole molecule. It happens especially in solutions where a negative ion will be attracted to the positive pole of the polar molecule while a positive ion will be attracted to the negative pole of the polar molecule. For example, it can be seen when sodium chloride dissolves in water, as illustrated in Figure1.9. Since sodium chloride is an ionic compound, and water is a polar molecule, the **ion-dipole interactions** are formed between the negative pole $O^{\delta-}$ of a water molecule and Na^+ cation, and also between the positive pole $H^{\delta+}$ of a water molecule and Cl^- anion.



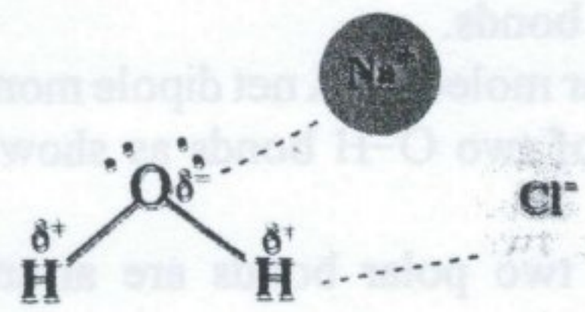


Figure 1.9 Ion-dipole Interaction in Aqueous Sodium Chloride Solution

London dispersion forces

The weakest intermolecular forces that can be formed between atoms, as well as non-polar molecules, are known as London dispersion forces, named after the German physicist Fritz London (1900 - 1954). Because of the constant motion of the electrons, an atom can develop a temporary (instantaneous) dipole when the electrons are distributed unsymmetrically about the nucleus. Then, this instantaneous dipole of the first atom can induce a second atom to be distorted because electrons repel one another. It leads to form a dipole in the second atom resulting in an electrostatic attraction between these two atoms. This electrostatic attraction is known as the **London dispersion force**, also called induced dipole-induced dipole interaction. Figure 1.10 represents the formation of the London dispersion forces between helium atoms as an example.

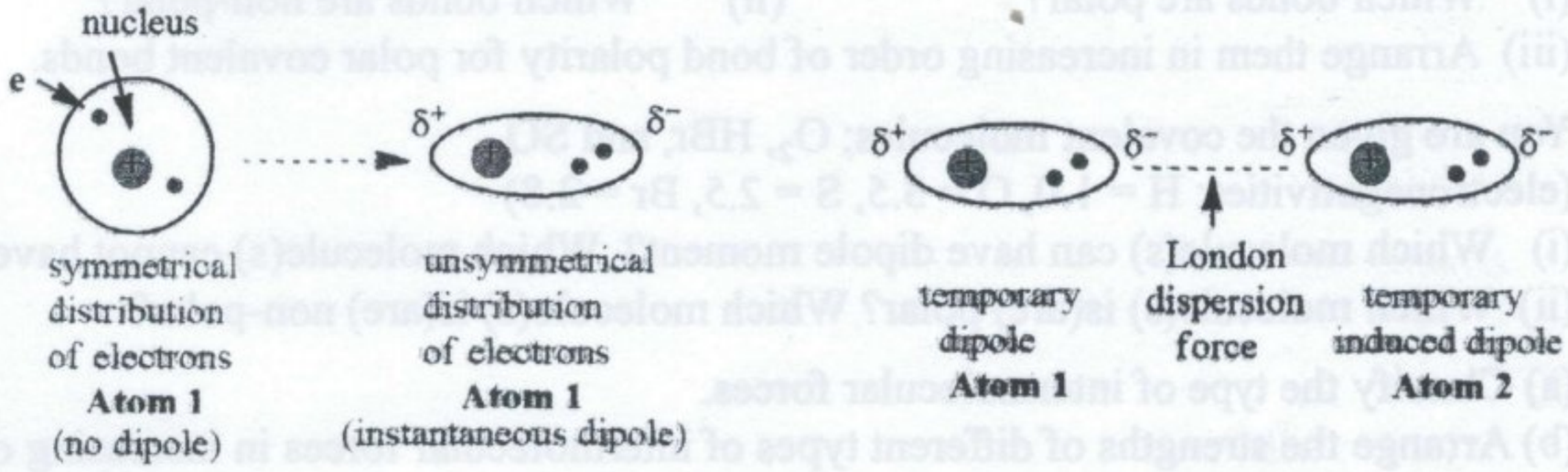


Figure 1.10 Formation of (a) Temporary Dipole of He Atom and (b) London Dispersion Force between Two He Atoms

These London dispersion forces can occur between non-polar molecules such as halogens, carbon dioxide, nitrogen, methane, and noble gases. Due to these weak attractive forces, non-polar substances can condense into liquids and can freeze into solids when the temperature is lowered sufficiently, e.g., liquid nitrogen and dry ice (solid CO_2). Hence, London dispersion forces are instantaneous dipole-dipole interactions that exist between all atoms and molecules, non-polar as well as polar.

(c) Hydrogen Bonding

The formation of hydrogen bonds between covalent molecules requires: (1) the first molecule has hydrogen attached to a high electronegative atom (F, O, or N) and (2) the second molecule possesses a lone pair of electrons on a small electronegative atom (F, O, or N). Because of the highly electronegativity difference between H atom and bonded F, O, or N atom, the bond is very highly polarised. The δ+ charge on the hydrogen atom is high enough for a bond to be formed with a lone pair of electrons on the F, O, or N atom of a neighbouring molecule.

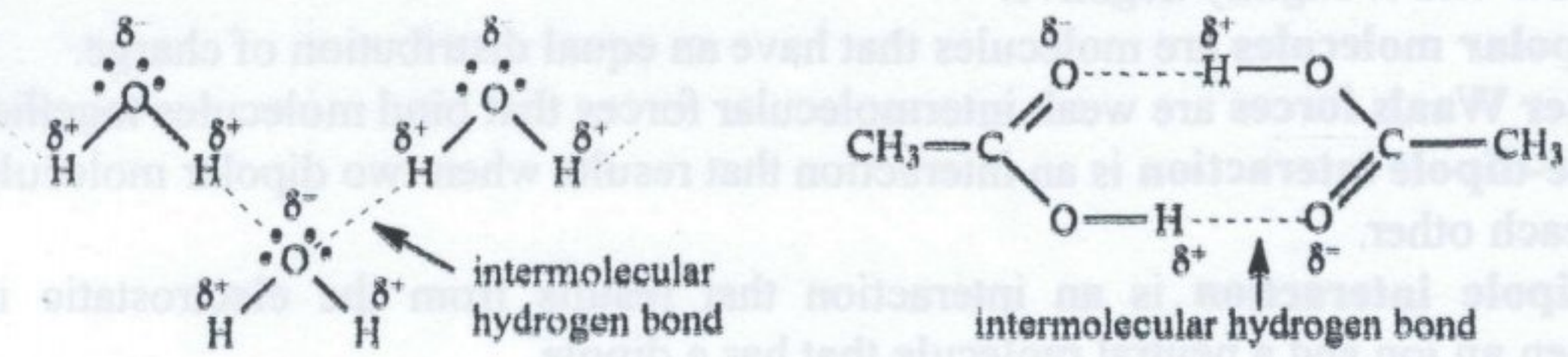


Figure 1.11 Intermolecular Hydrogen Bonds between (a) Water Molecules and

Figure 1.11 (a) shows the formation of **intermolecular hydrogen bonds** between water molecules, and Figure 1.11 (b) represents the formation of acetic acid dimer by intermolecular hydrogen bonds. Hydrogen bonding can occur as both intermolecular and intramolecular forces.

A hydrogen bond is a special type of dipole-dipole interaction that occurs between polar molecules and is stronger than van der Waals forces. The hydrogen bond is weaker than a covalent bond and is the strongest of all intermolecular forces.

REVIEW QUESTIONS

(1) You are given the following covalent bonds: C-Br, N-H, N-N, O-H, C-O, C-C.
(electronegativities: H = 1.0, C = 2.5, N = 3.0, O = 3.5, Br = 2.8)
(i) Which bonds are polar? (ii) Which bonds are non-polar?
(iii) Arrange them in increasing order of bond polarity for polar covalent bonds.

(2) You are given the covalent molecules; O_2, HBr, and SO_2.
(electronegativities: H = 1.0, O = 3.5, S = 2.5, Br = 2.8)
(i) Which molecule(s) can have dipole moment? Which molecule(s) cannot have?
(ii) Which molecule(s) is(are) polar? Which molecule(s) is(are) non-polar?

(3) (a) Classify the type of intermolecular forces.
(b) Arrange the strengths of different types of intermolecular forces in increasing order.
(c) Which one of the intermolecular forces (hydrogen bonding, dipole-dipole interaction, ion-dipole interaction, and London dispersion forces) exists in each of the following?
(i) aqueous KI solution (ii) CH_3OH (iii) N_2 (iv) HI

Key Terms

- **Intermolecular forces** are the forces between atoms, molecules, and ions when they are placed close to each other.
- **Polarity** is a separation of charge, leading to one part of a bond or molecule becoming positively charged and the other negatively charged.
- **Polar covalent bond** is a covalent bond in which the bonding electrons is unequally shared between two atoms.
- **Dipole** is a pair of charges that are equal in magnitude and opposite in charge that is separated by a distance.
- **Non-polar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms.
- **Dipole moment** is a measure of the polarity of a covalent bond.
- **Polar molecule** is a molecule in which one end of the molecule is slightly positive while the other end is slightly negative.
- **Non-polar molecules** are molecules that have an equal distribution of charge.
- **van der Waals forces** are weak intermolecular forces that bind molecules together.
- **Dipole-dipole interaction** is an interaction that results when two dipolar molecules interact with each other.
- **Ion-dipole interaction** is an interaction that results from the electrostatic interaction between an ion and a neutral molecule that has a dipole.

- **London dispersion force** is a temporary attractive force that results from the temporary dipoles formed due to the occupying positions of electrons in two adjacent atoms.
- **Hydrogen bonding** is the electrostatic attraction between a hydrogen atom in one polar molecule and a small electronegative atom (as of oxygen, nitrogen, or fluorine) in another molecule of the same or different polar substance.
- **Intermolecular hydrogen bonds** are the hydrogen bonds that occur between two atoms of same or different molecules.

1.5 METALLIC BONDING

Most of the metals are solids at room temperature, and therefore, there must be some sort of bonding between these metal atoms. These metal atoms are held together in solid crystalline form by a metallic bonding.

(a) Metallic Bonds

In a metallic bond, the atoms do not share or transfer electrons to bond together. The structure of a metallic bond is quite different from that of covalent or ionic bonds.

In metallic solids, e.g., sodium, magnesium, and aluminium, atoms of metals are present. They form metallic bonds. In a metallic bond, the valence electrons of the atoms are very loosely held, forming a common electron cloud. These valence electrons move freely within this electron cloud. These mobile electrons are often described as "a sea of electrons" which make the metals easily conduct electricity. The positively charged metallic nuclei are surrounded by free-moving electrons (Figure 1.12). The bonding results from the interaction of these electrons with the various nuclei. Hence, they are held together by a strong electrostatic attraction that results in low volatility of the metals.

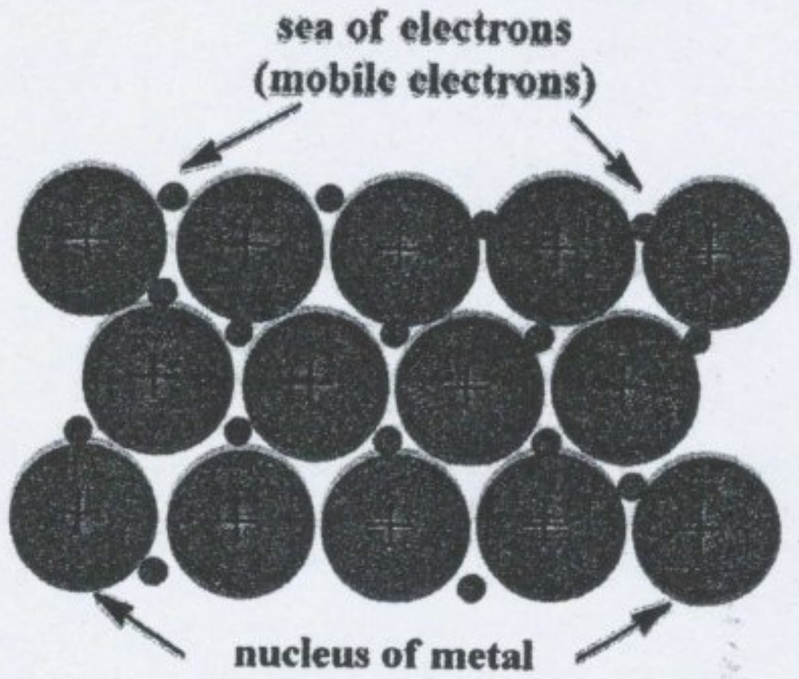


Figure 1.12 Metallic Bonding

(b) Strength of Metallic Bonding

Metals consist of giant structures of atoms that are packed closely together in a regular arrangement called a lattice. The strength of metallic bonding increases with (1) the increasing positive charge on the ions in the metal lattice, (2) the decreasing size of metal ions in the lattice, and (3) the increasing number of mobile electrons (valence electrons) per atom. However, the strength of metallic bond is lower than that of an ionic bond. Consequently, the melting points of some metals become lower compared with the ionic compounds.

REVIEW QUESTIONS

(1) Describe two everyday objects that contain the following chemical bonds:
(i) covalent bonds (ii) ionic bonds (iii) metallic bonds

(2) (a) Identify the type of bond existing in each of the following substances:
Zn, CCl_4, NaBr, Al, and $MgCl_2$.

Which of these substances will conduct electricity most effectively? Give a reason for your answer.

(b) Compare the strength of metallic bonding for the following pairs of metals:
(i) sodium and magnesium (ii) magnesium and calcium

(3) Tabulate the different types of bonding: ionic, covalent, and metallic bonding in terms of (i) types of elements involved, (ii) bond formation in terms of electrons, (iii) nature of the bond between atoms, (iv) bond strength (strong/weak), (v) melting point (high/low), and (vi) electrical conductivity (yes/no).

Chemistry in Society

- Common salt, an ionic compound is used as a food seasoning and preservative, in soap manufacturing, agriculture, water conditioning, wood preservative, de-icing agent, and many other uses. Sodium fluoride can be used in water fluoridation. Potassium iodide is added to "iodised" salt for thyroid health.
- Sodium, calcium, potassium, chloride, phosphate, and magnesium ions are all electrolytes that can be obtained from the foods we eat and the electrolyte beverages we drink.
- Metal salts such as strontium carbonate (red), calcium chloride (orange), sodium nitrate (yellow), barium chloride (green) and copper chloride (blue) are used in fireworks.

- Hydrogen bonding can occur in liquid water, solid ice, many biological structures of DNA and protein in our body, and cellulose in the tree trunk. Two strands of DNA are held together by hydrogen bonding.
- Spiders and geckos rely on van der Waals forces to walk up smooth walls.
- Dry ice (solid CO_2) is used in cold grinding, freeze drying, in cooling process for the chemical industry and the food industry. Liquid nitrogen is also used as a coolant.

EXERCISES

Q 1 to Q 4 (Understanding)

1. Write TRUE or FALSE for each of the following statements. If FALSE, correct it.
   (a) Chemical bonding occurs only by transferring valence electrons between the atoms involved in the bond.
   (b) To transfer a valence electron, the atom must have higher electronegativity than another atom.
   (c) The molecular shape of a water molecule, H_2O, is linear.
   (d) Beryllium chloride, $BeCl_2$, is a stable molecule that follows the octet rule.
   (e) Carbon tetrachloride, CCl_4, is a polar covalent molecule.
2. Fill in the blanks with a suitable word or phrase as necessary.
   (a) A bond's polarity is determined by the _____ of two bonded atoms.
   (b) In ionic compounds, the oppositely charged ions are held together by strong _____.

(c) The weak intermolecular forces that bind molecules together are known as _____.
(d) The shape of ammonia molecule is _____.
(e) The strength of metallic bonding increases with the decreasing size of the _____ ion in the lattice.

3. Choose the correct answer.
(a) The element having (a high electron affinity, high electron affinity and electronegativity, a high electronegativity) favours the formation of an anion.
(b) The electrons located in the outer shell of an atom are known as (valence electrons, valency, the sea of mobile electrons) of the atom.
(c) Nitrogen oxide, NO is a (polar, non-polar, triatomic) covalent molecule.
(d) In a diamond, each carbon atom is joined to (three, four, five) other carbon atoms forming a giant covalent structure.
(e) In the HCl molecule, there are (six, four, three) unshared pair electrons on the Cl atom.

4. Answer the following:
(a) (i) Why is chemical bonding important?
(ii) How can a chemical bond form between two atoms?
(b) (i) Write the complete electronic configuration for each of the following elements:
$_{6}C$; $_{17}Cl$; $_{15}P$; $_{12}Mg$; $_{18}Ar$; $_{16}S$; $_{19}K$
(ii) Write Lewis symbols for the following atoms: $_{3}Li$, $_{14}Si$, $_{15}P$, $_{10}Ne$, $_{18}Ar$.
(iii) What do Lewis symbols for atoms show?
(c) Classify the types of intermolecular forces and arrange their strengths in increasing order.

Q 5 to Q 11 (Analysing and Problem Solving)

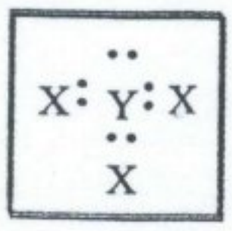
5. (a) Using Lewis structures, show how ionic bond formed between the elements in each of the following pairs:
(i) $_{19}K$ and $_{35}Br$ (ii) $_{20}Ca$ and $_{17}Cl$
(b) Describe the formation of magnesium fluoride compound using Lewis symbols.
(c) Briefly discuss the structure of solid sodium chloride.

6. (a) What would happen when two hydrogen atoms are approaching one another?
(b) Explain how the covalent bonding takes place in a molecule.
(c) Arrange the single, double and triple bonds in increasing order of bond length and bond strength. Give reasons for your answers.

7. (a) What are the differences between covalent bonding and coordinate bonding? Explain with examples.
(b) Explain the formation of hydronium ion using the Lewis structure.

8. (a) How do you understand the VSEPR theory?
(b) Draw the Lewis structures and predict the molecular shapes for BF_3 and CF_4.

9. Given the following Lewis structure, where **X** and **Y** each represents a different element.



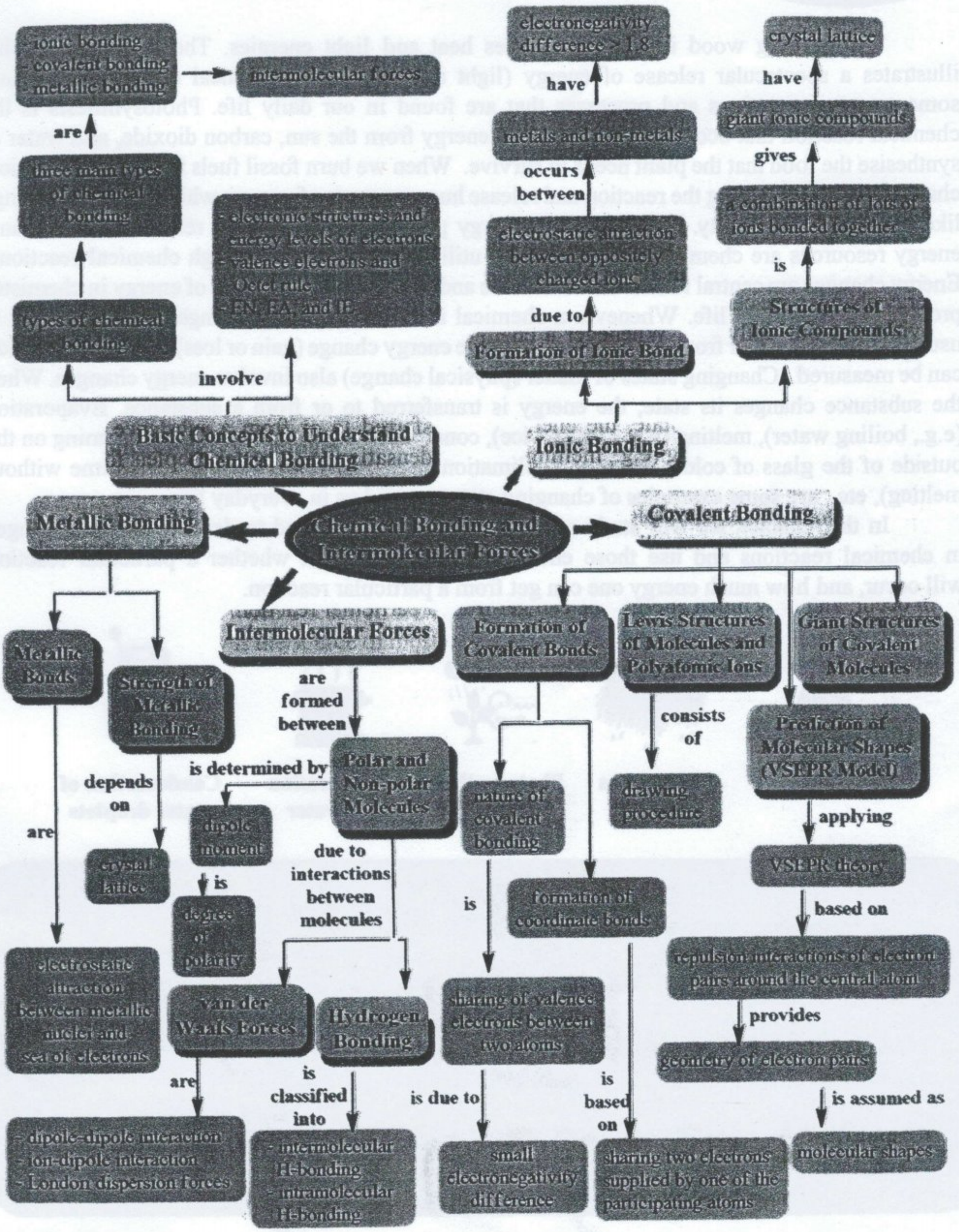
(i) What is the valency of **X**?
(ii) What is the valency of **Y**?
(iii) What elements would **X** and **Y** represent?
(iv) Name the molecule formed from **X** and **Y**.

10. (a) What are the differences between polar and non-polar molecules?
    (b) Compare the polarity of each of the following pairs of molecules.
    (i) H_2O and CO_2 (ii) CCl_4 and $CHCl_3$
11. Describe the molecular conditions necessary for the existence of a (i) dipole-dipole interaction, (ii) London dispersion force, and (iii) hydrogen bonds.

Q 12 to Q 19 (Applying and Critical Thinking)

12. (a) What are the differences between metallic bonding and ionic bonding?
    (b) Explain that metals can conduct electricity but solid ionic compounds cannot conduct.
    (c) Which metal has the higher melting point in the given substances - divalent or trivalent metals? Give a reason for your answer.
13. Magnesium nitride, Mg_3N_2, is produced when nitrogen gas is passed over red-hot magnesium metal.
    (i) Identify the type of the compound. Give a reason for your answer.
    (ii) Describe the formation of the compound using the Lewis symbols and Lewis structure.
    (iii) Does the compound have a high or low melting point? Give a reason for your answer.
14. Three elements: $_{13}X$, $_9Y$, and $_{17}Z$ are given. (electronegativities: X = 1.5 , Y = 4.0 , Z = 3.0)
    (i) What type of compound is formed between the given pairs: $_{13}X$ and $_9Y$, and $_{13}X$ and $_{17}Z$?
    (ii) Give a Lewis dot structure for each compound.
    (iii) Give the possible formula of each of the unknown compounds.
    (iv) Predict the molecular shape of a covalent molecule.
15. What happens when ammonia combines with boron trifluoride? Explain briefly.
16. How do you draw the Lewis structures for the following molecules?
    (i) PF_3 (ii) PF_5 (iii) SF_4 (iv) SF_6 (v) $AlBr_3$ (vi) NO (vii) IF_3
    Which of these molecules are electron-deficient molecules?
    Which of these molecules are expanded valence shell molecules?
17. Predict the shapes of CH_4, NH_3, and H_2O molecules with explanation.
18. Draw the Lewis structures and indicate the types of chemical bonding existing in each of the following substances:
    (i) Na_2CO_3 (ii) $(NH_4)_2SO_4$ (iii) NH_4Cl (iv) KOH
19. Identify the chemical bonding between atoms, and intermolecular forces existing in the following substances with appropriate diagrams.
    (a) SO_2 (b) KOH aqueous solution (c) I_2 (d) dry ice, CO_2 (e) Ne

CHAPTER REVIEW
(Concept Map)



CHAPTER 2

ENERGY CHANGES IN CHEMICAL REACTIONS

The burning wood in the air releases heat and light energies. The fireworks display illustrates a spectacular release of energy (light and heat) in a chemical reaction. There are some common reactions and processes that are found in our daily life. Photosynthesis is the chemical reaction that occurs when plants use energy from the sun, carbon dioxide, and water to synthesise the food that the plant needs to survive. When we burn fossil fuels for energy, chemical changes take place during the reaction and release huge amounts of energy, which we use for things like power and electricity. Except for the energy produced from nuclear reactors, all of man's energy resources are chemicals or involve the utilisation of energy through chemical reactions. Energy changes are central to chemical reactions and understanding the role of energy in chemistry provides for our daily life. Whenever a chemical reaction (chemical change) occurs, energy is usually transferred to or from the surroundings. The energy change (gain or loss) during the reaction can be measured. Changing states of matter (physical change) also involve energy changes. When the substance changes its state, the energy is transferred to or from a substance. Evaporation (e.g., boiling water), melting (e.g., melting ice), condensation (e.g., water droplets forming on the outside of the glass of cold beverage), sublimation (e.g., mothball and dry ice sublime without melting), etc., are some examples of changing states around us in everyday life.

In this chapter, we will study some important terms needed to describe energy changes in chemical reactions and use those energy changes to predict whether a particular reaction will occur, and how much energy one can get from a particular reaction.

Burning woods

Fireworks

Photosynthesis

Evaporation of water

Condensation of water droplets

Learning Outcomes

After completing this chapter, students will be able to:

- explain how changes in energy during chemical reactions
- identify the reactions as spontaneous or non-spontaneous, and exothermic or endothermic
- use the concept of energy in bond breaking and bond making
- differentiate the enthalpy and enthalpy changes of chemical reactions
- discuss the types of enthalpy changes of reactions and measure enthalpy changes
- apply Hess's law to construct enthalpy cycles and calculate enthalpy changes of reactions
- calculate the enthalpy change of a reaction using bond energy (bond enthalpy)

2.1 ENERGY CHANGES

There are various kinds of energy such as kinetic energy (due to the movement), potential energy (due to the position), electrical energy, light energy, thermal energy, chemical energy, mechanical energy, etc. In addition, energy can neither be created nor destroyed as stated in the **Law of Conservation of Energy**. However, energy can change from one form to another without a net loss or gain of energy and it is called **energy transformation**. Energy transformations occur everywhere in daily life. Some common energy transformation devices are as follows:

- electric motor (electrical energy into kinetic energy)
- hair dryer (electrical energy into thermal energy)
- battery (chemical energy into electrical energy)
- automobile engine (chemical energy into mechanical energy)
- solar cell (light energy into electrical energy)

Moreover, all chemical reactions involve energy changes. Whether a chemical reaction absorbs or releases energy, the overall energy is not changed during the reaction.

(a) Chemical Energy Changes

Chemical energy is the energy that is stored in the bonds of chemical compounds such as atoms and molecules. Energy changes take place during chemical reactions. In some reactions, the energy changes can be observed as either an increase or a decrease in the overall energy of the system. In some reactions, it can be seen as a change in the temperature. In other reactions, this change can be observed when a reaction starts to give off light.

Chemical energy is the source of most of the energy that humans need to function. Humans release this chemical energy during digestion and use it to power systems inside the body. Plants store chemical energy in carbohydrates formed during photosynthesis. Energy changes are very important in chemistry because almost all reactions involve a change in energy. Whenever a chemical reaction takes place between reactants to form products, there is always an energy change usually in the form of heat. Thus, chemical reactions often involve changes in energy due to the breaking and formation of bonds.

The energy change is due to the difference in the amounts of stored chemical energy between the reactant and the product particles in a chemical reaction. The interactions between particles can produce cooling or heating effects that are used in everyday applications. When an instant cold pack and a hot pack have been activated, the change in temperatures occurs. These temperature changes are due to a solid substance (salt) dissolving in water. This generates a chemical reaction. These packs contain a mixture of chemicals that react together to create heat and cold. A chemical reaction involves the breaking of bonds in the reactants and the forming of bonds in the products. In the given examples of cold and hot packs, energy is absorbed to break bonds, and energy is released when bonds are formed during the process of dissolving.

Chemical reactions provide electricity which is the result of interactions between ions in an electrolyte. Examples are batteries and fuel cells.

(b) Changes of Energy in Chemical Reactions

Some reactions take place on their own under a given set of conditions, and some are needed to provide energy for the reaction to proceed. A process that can take place on its own accord is called spontaneous. Non-spontaneous processes need the energy to take place. As mentioned in the introduction of Section 2.1, almost all chemical reactions absorb or release energy, generally in the form of heat. Depending on the gain or loss of energy (heat), chemical reactions can be classified as endothermic or exothermic.

(i) Spontaneous and non-spontaneous reactions

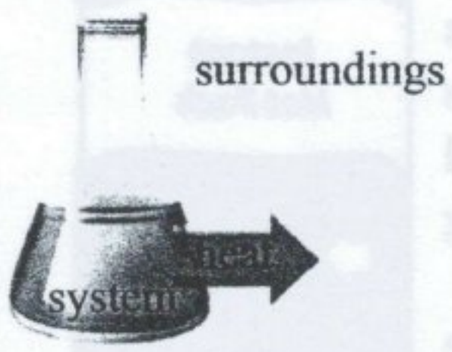
In a spontaneous reaction, the physical or chemical change occurs without the addition of energy. Adding a solution of dilute sulphuric acid to a solution of sodium hydroxide is an example of a spontaneous reaction because the reaction takes place without any energy being added.

The reaction between magnesium and oxygen, and the reaction between copper and oxygen are both non-spontaneous reactions. They need the energy to initiate the reaction. Most of the reaction will not take place until the system has some minimum amount of energy added to it. After the reaction has started, it may then carry on spontaneously. Iron rusting is exothermic and spontaneous. When the ice melts at room temperature, that is a spontaneous and endothermic process.

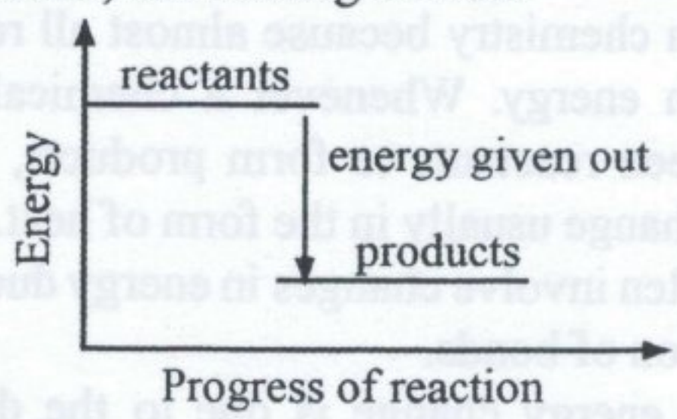
(ii) Exothermic and endothermic reactions

Exothermic reactions

When sulphuric acid is slowly poured into water, the flask or beaker becomes hot. This is heat being released to the **surroundings** by the reacting **system**. This kind of change (reaction) is known as an **exothermic reaction**. Examples of exothermic reactions are burning candle, the combustion of a fuel, the neutralisation reaction, respiration, and rusting of iron.



Exothermic reaction

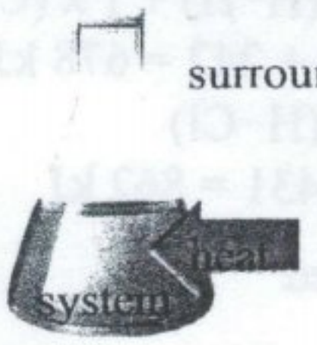


Energy level diagram for exothermic reaction
(reactants ⟶ products + energy)

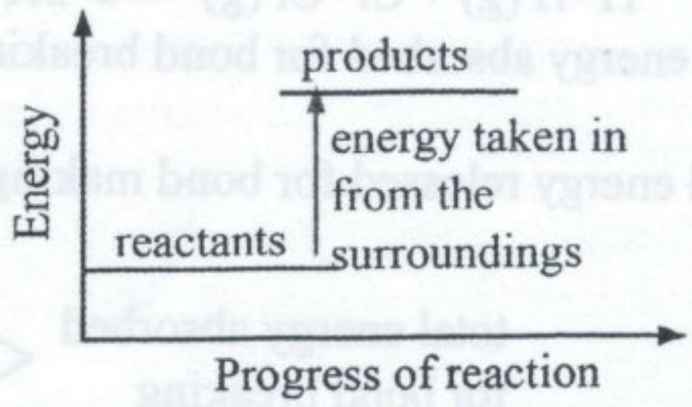
Exothermic reactions give out energy. So, there is a temperature rise. In exothermic reactions, the energy of the product is lower than the energy of the reactants because energy has been released during the reaction. This is shown on the energy level diagram.

Endothermic reactions

When ammonium chloride is dissolved in water, the flask becomes quite cold to the touch. This is heat being absorbed from the surroundings by the reacting system. This kind of change (reaction) is known as an **endothermic reaction**. Examples of endothermic reactions are melting of ice, cooking an egg, evaporating liquid water, and thermal decomposition of limestone.



Endothermic reaction



Energy level diagram for endothermic reaction

(reactants + energy ⟶ products)

Endothermic reactions take in energy from the surroundings. So, there is a temperature fall. In endothermic reactions, the energy of the products is higher than the energy of the reactants because energy has been absorbed during the reaction. This is shown on the energy level diagram.

Energy transfer in chemical reactions

Energy changes in chemical reactions are caused by the making and breaking of chemical bonds. In a chemical reaction, bonds in the reactants must be broken first. Energy is absorbed to break bonds. Bond breaking is an endothermic process. Then new bonds in the products form. Energy is released when new bonds form. Bond making is an exothermic process. For example, when nitrogen reacts with oxygen to form nitrogen oxide, the bonds between the nitrogen molecules and oxygen molecules must first be broken to form atoms of nitrogen and oxygen. Nitrogen atoms then form bonds with oxygen atoms, forming nitrogen oxide (Figure 2.1).

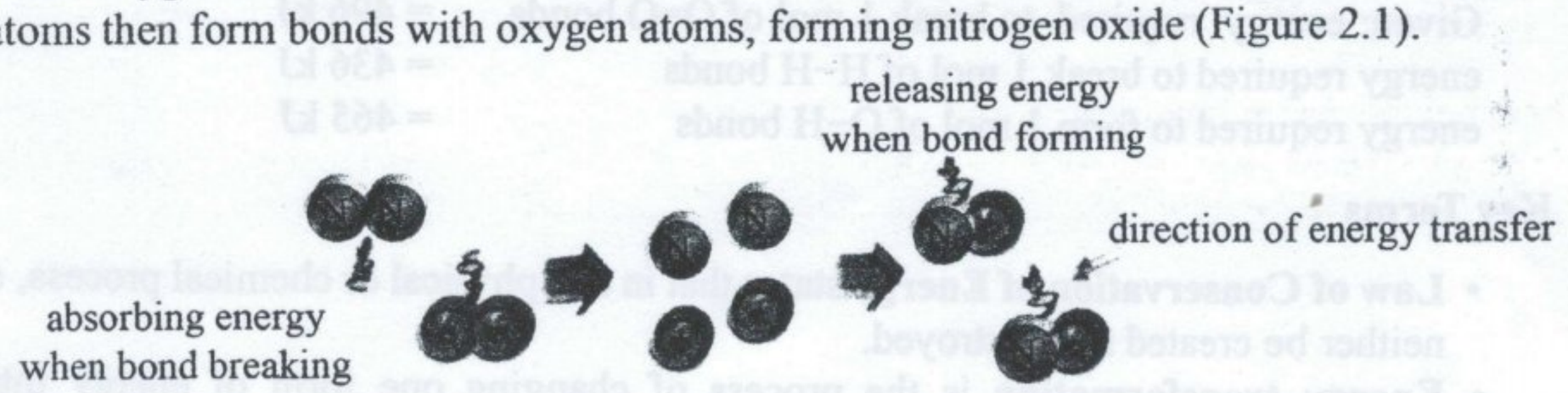


Figure 2.1 Energy Transfer Caused by Bond Breaking and Bond Making in a Chemical Reaction

As mentioned in Section 2.1 (a), if the energy absorbed in bond breaking is less than the energy given out in bond making, the reaction is exothermic. If the energy absorbed in bond breaking is more than the energy given out in bond making, the reaction is endothermic.

In an exothermic reaction: total energy absorbed for bond breaking < total energy released for bond making

In an endothermic reaction: total energy absorbed for bond breaking > total energy released for bond making

Example 1: Predict whether the following reaction is exothermic or endothermic.

$$H_2\,(g) + Cl_2\,(g) \longrightarrow 2HCl\,(g)$$

Given: energy required to break 1 mol of H–H bonds = 436 kJ
energy required to break 1 mol of Cl–Cl bonds = 242 kJ
energy required to make 1 mol of H–Cl bonds = 431 kJ

Solution: $H–H\,(g) + Cl–Cl\,(g) \longrightarrow 2H–Cl\,(g)$

total energy absorbed for bond breaking (energy in) = 1 x (H–H) + 1 x (Cl–Cl)
= 436 + 242 = 678 kJ

total energy released for bond making (energy out) = 2 x (H–Cl)
= 2 x 431 = 862 kJ

total energy absorbed for bond breaking < total energy released for bond making

678 kJ < 862 kJ

Therefore, the reaction is exothermic.

REVIEW QUESTIONS

(1) What energy transformation takes place in each of the following?
(i) electric bulbs (ii) fuel cells (iii) electric generator (iv) steam boiler (v) gas turbine

(2) Predict whether each reaction takes place exothermic or endothermic reaction.
(i) burning of a candle (ii) digestion of food (iii) cooking an egg
(iv) condensation (v) cracking alkanes

(3) Is this reaction exothermic or endothermic?

$$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l)$$

Given: energy required to break 1 mol of O=O bonds = 496 kJ
energy required to break 1 mol of H–H bonds = 436 kJ
energy required to form 1 mol of O–H bonds = 465 kJ

Key Terms

- **Law of Conservation of Energy** states that in any physical or chemical process, energy can neither be created nor destroyed.
- **Energy transformation** is the process of changing one form of energy into another.
- **System** is the specific part of the universe that contains the reaction or process which is studied.
- **Surroundings** are everything in the universe other than the system.
- **Exothermic reaction** is a reaction which releases heat into the surroundings.
- **Endothermic reaction** is a reaction which absorbs heat from the surroundings.

2.2 ENTHALPY CHANGES IN CHEMICAL REACTIONS

The total chemical energy of a substance is called its enthalpy (or heat content). **H** is the symbol for enthalpy. In chemical reactions, there are changes in chemical energy and therefore, enthalpy changes. The heat change of a chemical reaction is usually expressed by the terms "change in heat content" or "change in enthalpy" of the chemical reaction. The change in enthalpy describes the amount of heat transferred at constant pressure during a chemical reaction. Heat changes can be measured by using a calorimeter.

(a) Enthalpy Changes and Standard Enthalpy Changes

The heat absorbed or released in a process occurring at constant pressure is called the **enthalpy change**; it is given the symbol ΔH. The unit of enthalpy change is kilojoule per mole (kJ mol^{-1}). Hence, the ΔH value gives the amount of energy that is absorbed or released per mole of the product formed. In other words, ΔH is the difference in the heat content of the products and reactants. Enthalpy is not measured directly, however, the change in enthalpy is measured, which is the heat added or lost by the system. The change in enthalpy can be expressed as

$$\Delta H = H_{products} - H_{reactants}$$

For an endothermic reaction where energy is absorbed from the surroundings, the total energy of the products is greater than that of the reactants, then ΔH is positive, i.e., a positive sign. For example,

$$\tfrac{1}{2} N_2 (g) + \tfrac{1}{2} O_2 (g) \longrightarrow NO (g) \qquad \Delta H = (+)$$

For an exothermic reaction where energy is released to the surroundings, the total energy of the products is less than that of the reactants, then ΔH is negative, i.e., a negative sign.
For example,

$$NaOH (aq) + HCl (aq) \longrightarrow NaCl (aq) + H_2O (l) \qquad \Delta H = (-)$$

The enthalpy of a reaction depends on the conditions under which the reaction is carried out. Therefore, it is necessary to specify some standard conditions.

The heat absorbed or released in a process occurring at standard conditions of temperature and pressure is called the standard enthalpy change, ΔH^{θ}. The standard conditions chosen for energy changes are as follows:

standard temperature = 25 °C = 298 K
standard pressure = 1 atm = 760 mmHg = 101 kPa

(i) Writing thermochemical equations

A thermochemical equation is a balanced chemical equation that includes the physical states of all reactants and products and the standard enthalpy change (ΔH^{θ} is negative or positive). Sometimes, the thermochemical equation may be shown the enthalpy change ΔH rather than ΔH^{θ}. It is important to include the physical states of the reactants and products in the thermochemical equation because the value of enthalpy change depends on those states. It is usual to indicate the physical state of each substance by the appropriate letter places in brackets after the formula; (s) for solid, (l) for liquid and (g) for gas. Some examples of thermochemical equations are

$$HgO (s) \longrightarrow Hg (l) + \tfrac{1}{2} O_2 (g) \qquad \Delta H = +90.7 \text{ kJ mol}^{-1}$$

$$C (\text{graphite}) + O_2 (g) \longrightarrow CO_2 (g) \qquad \Delta H^{\theta} = -394 \text{ kJ mol}^{-1}$$

(ii) Standard enthalpy changes of reactions

The standard enthalpy change is expressed in different ways depending on the nature of the reaction. In more general cases, it can use the term, standard enthalpy change of reaction.

The standard enthalpy change of a reaction (ΔH_r^{θ}) is the enthalpy change when the molar quantities of reactants stated in the chemical equation react to give products under standard conditions.

The enthalpy changes of the reaction can be exothermic or endothermic and ΔH_r^θ can be positive or negative. For example,

$$H_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_r^\theta = -286 \text{ kJ mol}^{-1}$$

The usual standard enthalpy changes for chemical reactions are the standard enthalpy change of formation, the standard enthalpy change of combustion, and the standard enthalpy change of neutralisation.

Standard enthalpy change of formation, ΔH_f^θ

The standard enthalpy change of formation of a compound is the enthalpy change when one mole of a compound is formed from its elements under standard conditions.

The formation of a compound can be exothermic or endothermic and ΔH_f^θ can be positive or negative. For example,

$$\tfrac{1}{2} N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H_f^\theta\ [NO_2(g)] = +33 \text{ kJ mol}^{-1}$$

$$C \text{ (graphite)} + \tfrac{1}{2} O_2(g) \longrightarrow CO(g) \qquad \Delta H_f^\theta\ [CO(g)] = -110 \text{ kJ mol}^{-1}$$

Note that the state symbol for carbon is shown as "graphite". This is because there are several forms of carbon but the most stable is graphite and choose the most stable form when writing chemical equations where enthalpy changes are shown.

Standard enthalpy change of combustion, ΔH_c^θ

The standard enthalpy change of combustion is the enthalpy change when one mole of a substance (element or compound) is burnt completely in oxygen under standard conditions.

Combustion reactions are always exothermic and the enthalpy changes are always negative. For example,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c^\theta\ [CH_4(g)] = -891 \text{ kJ mol}^{-1}$$

Standard enthalpy change of neutralisation, ΔH_n^θ

The standard enthalpy change of neutralisation is the enthalpy change when solutions of an acid and an alkali react together under standard conditions to produce one mole of water.

The neutralisation reaction is exothermic and the enthalpy change is negative. For example,

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) \qquad \Delta H_n^\theta = -57.1 \text{ kJ mol}^{-1}$$

Example 2: Write down the thermochemical equations for the following reactions.

(i) Combustion of carbon (graphite) ($\Delta H_c^\theta = -394$ kJ mol^{-1})

(ii) Combustion of methane gas ($\Delta H_c^\theta = -891$ kJ mol^{-1})

(iii) Combustion of ethanol ($\Delta H_c^\theta = -1367$ kJ mol^{-1})

(iv) Formation of ethanol ($\Delta H_f^\theta = -235$ kJ mol^{-1})

(v) Formation of $NaHCO_3$ (s) ($\Delta H_f^\theta = -951$ kJ mol^{-1})

Solution:

(i) $C\ (graphite) + O_2\ (g) \longrightarrow CO_2\ (g)$ $\quad \Delta H_c^\theta = -394\ kJ\ mol^{-1}$

(ii) $CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l)$ $\quad \Delta H_c^\theta = -891\ kJ\ mol^{-1}$

(iii) $C_2H_5OH\ (l) + 3O_2\ (g) \longrightarrow 2CO_2\ (g) + 3H_2O\ (l)$ $\quad \Delta H_c^\theta = -1367\ kJ\ mol^{-1}$

(iv) $2C\ (graphite) + 3H_2\ (g) + \frac{1}{2}O_2\ (g) \longrightarrow C_2H_5OH\ (l)$ $\quad \Delta H_f^\theta = -235\ kJ\ mol^{-1}$

(v) $Na\ (s) + C\ (graphite) + \frac{1}{2}H_2\ (g) + \frac{3}{2}O_2\ (g) \longrightarrow NaHCO_3\ (s)$ $\quad \Delta H_f^\theta = -951\ kJ\ mol^{-1}$

(b) Measurement of Enthalpy Changes

The enthalpy changes ΔH (heat changes) of reactions can be measured in several ways. Experimentally, ΔH is not measured. The heat change, q, is measured by using the following equation:

$$q = mc\Delta T$$

If the mass of the reactants (m), the change in temperature (ΔT) and the specific heat of materials (c) are known, q can be calculated. Since the measurements are performed under constant pressure, ΔH is equal to the q measured. The heat changes related to the physical changes involve melting, evaporation, etc., and chemical changes including burning, acid-base reaction, neutralisation reaction, etc. can be measured by the calorimeter. A calorimeter is a device to measure the amount of heat released or absorbed in reactions that occur in solutions. The heat change can be measured through the thermometer.

Enthalpy changes of reactions in solution

The enthalpy change of solution, ΔH_{sol}, of a substance, is the enthalpy change when one mole of the substance is dissolved in water. The simplest way of measuring enthalpy change is to use the energy to heat (or cool) water or a solution. The following measurements are needed to make:

- the mass of the reactants
- the mass of water, **m** (or its volume, since its density is 1.00 g cm^{-3})
- the rise (or fall) in temperature of the water or solution, **ΔT**

In the calorimeter, to find the heat change of a substance, the sample is added to a calorimeter and the initial and the final temperature of the reaction is recorded.

The heat change, **q**, can be calculated by the following equation:

$$q = mc\Delta T$$

where q = the heat change, m = the mass of water, c = the specific heat capacity of water, ΔT = rise (or fall) in temperature of the water or solution ($\Delta T = T_{final} - T_{initial}$).

The amount of heat needed to raise the temperature of one gram of water by one degree is known as the **specific heat capacity** of water and is given the symbol c. It has a value of 4.18 J g^{-1} $°C^{-1}$. If ΔT is positive value (i.e., $T_{final} > T_{initial}$), the q value will also be positive. Although q = ΔH, the reaction is giving off this amount of energy. Thus, the actual sign on ΔH is negative (–).

Figure 2.2 shows a basic calorimeter used for the measurement of heat change.

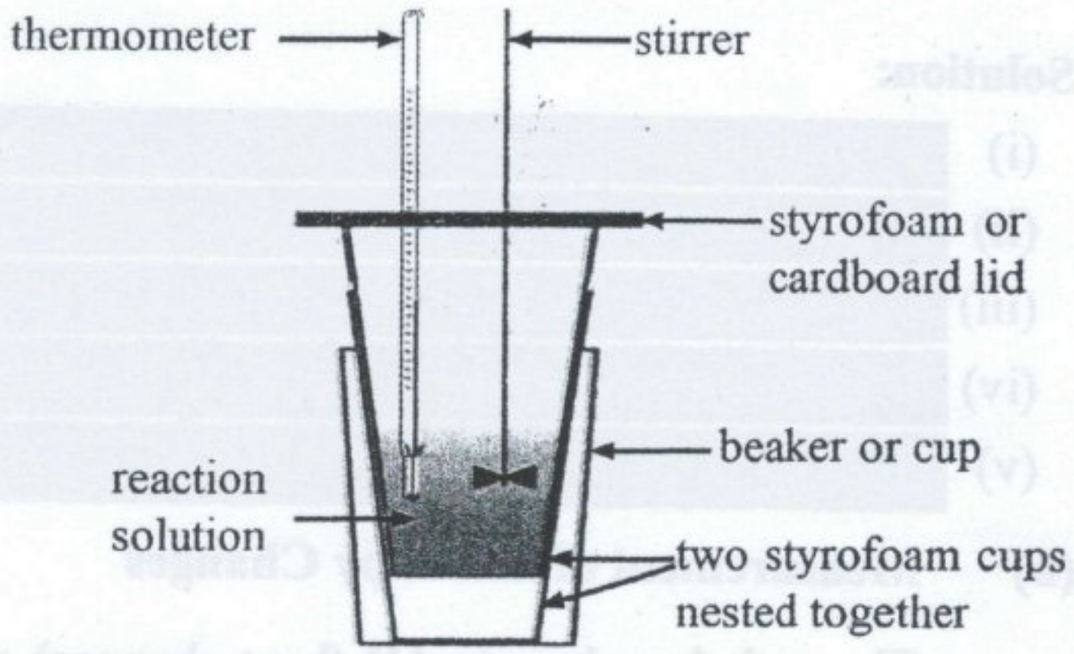


Figure 2.2 A Basic Calorimeter Used for Simple Heat Measurement of Reactions in Solution

Example 3: A known amount of water is placed in the calorimeter and the initial temperature is measured. The finely powdered solid ammonium nitrate is weighed and added into the water. The water is stirred until all the solid has dissolved, and the lowest temperature is recorded. The following results were obtained.

mass of water (m) = 100 g
specific heat capacity of water (c) = 4.18 J g^{-1} $°C^{-1}$
mass of ammonium nitrate = 7.10 g
initial temperature = 18.2 °C
final temperature = 12.8 °C

Calculate the enthalpy change of ammonium nitrate solution. (N=14, H=1, O=16)

Solution:

$$q = mc\Delta T$$
$$= 100 \times 4.18 \times (12.8 - 18.2) \text{ } (\Delta \text{ means "final – initial"})$$
$$= -2257 \text{ J} = -2.257 \text{ kJ}$$

Since $T_{final} < T_{initial}$ the heat is absorbed. Thus, the reaction is endothermic and the enthalpy change is positive.

molar mass of $NH_4NO_3 = 14 + (4x1) + 14 + (3x16) = 80 \text{ g mol}^{-1}$

$$\text{the heat absorbed} = \frac{2.257 \text{ kJ}}{7.10 \text{ g}} \times \frac{80 \text{ g}}{1 \text{ mol}}$$
$$= 25.43 \text{ kJ mol}^{-1}$$

$$\therefore \Delta H_{sol} = +25.43 \text{ kJ mol}^{-1}$$

Example 4: In an experiment, a known amount of acid in solution (50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid) is placed in a calorimeter and its temperature is recorded. An equivalent amount of base (50 cm^3 of 2.0 mol dm^{-3} sodium hydroxide solution) is added and the temperature rise is measured. Assuming that the resultant solution is the dilute solution. Calculate the enthalpy change of neutralisation, ΔH_n.

Given:
initial temperature of HCl = 17.5 °C
initial temperature of NaOH = 17.9 °C
final temperature = 31.0 °C
The specific heat capacity of water is 4.18 J g^{-1} $°C^{-1}$.

Solution:

Average temperature of the HCl and NaOH = (17.5+17.9)/2 = 17.7 °C

$q = mc\Delta T$

$= (50 + 50) \times 4.18 \times (31.0 - 17.7) = 5559 \text{ J} = 5.559 \text{ kJ}$

Since $T_{final} > T_{initial}$ the heat is released. Thus, the reaction is exothermic and the enthalpy change is negative.

$$\text{mol of HCl} = \text{mol of NaOH} = 50 \text{ cm}^3 \times \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} \times \frac{2 \text{ mol}}{1 \text{ dm}^3} = 0.10 \text{ mol}$$

When 0.10 mole of HCl and 0.10 mole of NaOH produce 0.10 mole of water, 5.559 kJ of heat is released.

∴ the heat released for one mole of water is 55.59 kJ mol^{-1}.

$$\text{the heat released} = \frac{5.559 \text{ kJ}}{0.10 \text{ mol}} = 55.59 \text{ kJ mol}^{-1}$$

$$\therefore \Delta H_n = -55.59 \text{ kJ mol}^{-1}$$

Note: It can take the average temperature because the volumes of acid and base solutions are equal. Because the solution is very dilute, its specific heat capacity is taken to be the same as that of water.

Bomb calorimeter

A bomb calorimeter is a type of calorimeter for determining the heat of combustion by igniting a sample in a high pressure of oxygen in a sealed vessel and measuring the resulting temperature rise. The highly accurate values of the standard enthalpy change of combustion (ΔH_c^0) can be measured only by a bomb calorimeter. It is used to measure the energy content of fuels.

REVIEW QUESTIONS

(1) The formation of nitrogen dioxide (NO_2) from a reaction of nitrogen with oxygen in the car engines have a ΔH value of + 33.2 kJ mol^{-1}.
   (i) Write a chemical equation for the reaction. (ii) Is the reaction exothermic or endothermic?
   (iii) What types of energy changes are involved in bond breaking and bond forming?

(2) Write down the thermochemical equations indicating the sign of the enthalpy change for the following processes:
   (i) One mole of methane gas is completely burned in oxygen.
   (ii) 0.1 mol dm^{-3} of hydrochloric acid is neutralised with 0.1 mol dm^{-3} of potassium hydroxide solution.
   (iii) Solid ammonium chloride is dissolved in water.

(3) Classify each of the following reactions as ΔH_f^θ, ΔH_c^θ , ΔH_n^θ, or ΔH_{sol}^θ.

   (i) $C \text{ (graphite)} + O_2 \text{ (g)} \longrightarrow CO_2 \text{ (g)}$ (ii) $HCl \text{ (aq)} + NaOH \text{ (aq)} \longrightarrow NaCl \text{ (aq)} + H_2O \text{ (l)}$

   (iii) $NaCl \text{ (s)} + H_2O \text{ (l)} \longrightarrow NaCl \text{ (aq)}$ (iv) $2C \text{ (graphite)} + 3H_2 \text{ (g)} + \frac{1}{2} O_2 \text{ (g)} \longrightarrow C_2H_5OH \text{ (l)}$

Key Terms

- **Enthalpy change** is the heat change accompanying a chemical reaction at constant pressure.
- **Specific heat capacity** of liquid is the energy required to raise the temperature of 1 g of liquid by 1 °C.

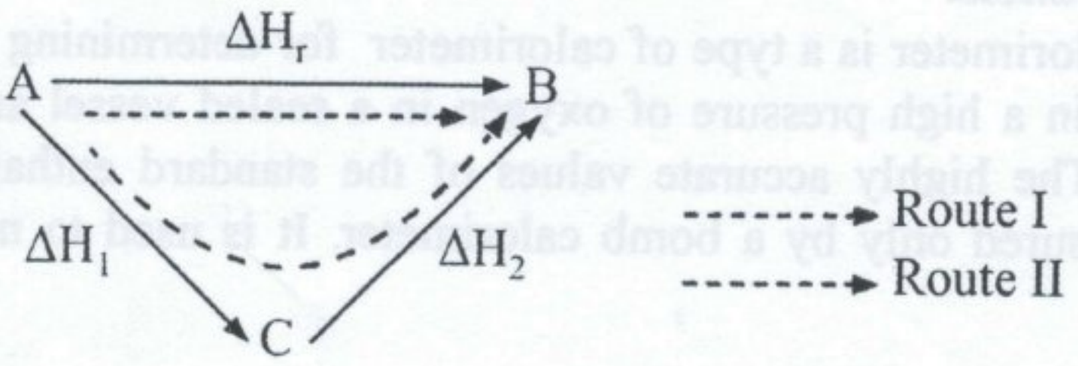
2.3 HESS'S LAW

There are very few reactions whose enthalpy change can be measured directly by measuring the change in temperature in a calorimeter. In some cases, the reaction is difficult, even impossible, to carry out individually. By using Hess's law, the enthalpy change for such reactions can be determined indirectly. Hess's law can be stated as below.

The enthalpy change for a chemical reaction is the same, whatever route is taken from reactants to products.

(a) Enthalpy Cycle

Hess's law can be illustrated by drawing an enthalpy cycle. For example, the reactant A directly forms B. This is the Route I. In Route II, reactant A forms C, and C is changing into B. According to Hess's law, the enthalpy changes of Route I are the same as for Route II. The enthalpy cycle for different routes of the reaction is shown as follows:



According to Hess's law,

Enthalpy change of Route I = Enthalpy changes of Route II

$$\Delta H_r = \Delta H_1 + \Delta H_2$$

If there are more than two steps in Route II, the enthalpy changes of the reaction can be expressed as

$$\Delta H_r = \Delta H_1 + \Delta H_2 + \Delta H_3 + \ldots$$

Constructing the enthalpy cycle

The enthalpy cycle can be constructed in the following steps:

Step (1) Write down the equation for the enthalpy change of the reaction.

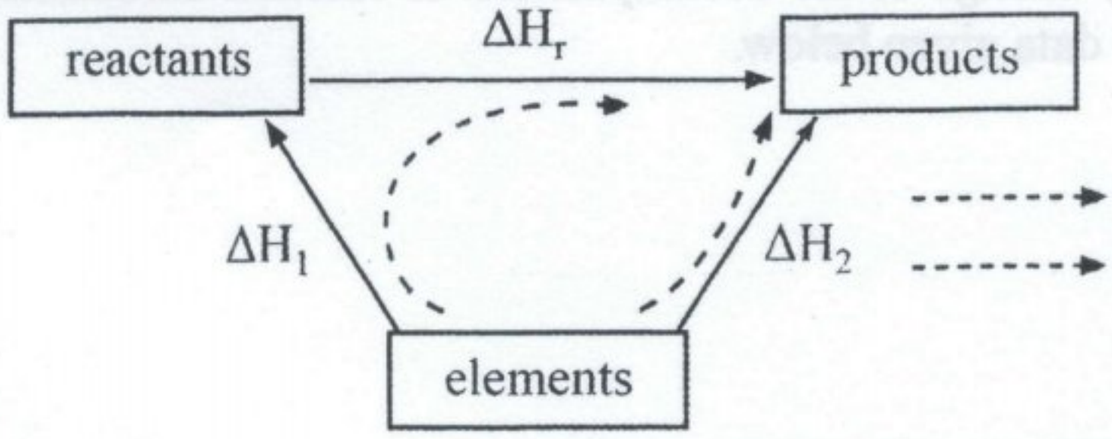
Step (2) Based on the data given, draw the enthalpy cycle with the correct arrow direction.

Step (3) Write the corresponding symbols for enthalpy changes over the arrows.

Step (4) Find two routes (clockwise and anticlockwise) and apply Hess's law to calculate the required enthalpy change (i.e., Route I is equal to Route II). For calculation, take into account the number of moles of each reactant and product. Note that the standard enthalpy change for the formation of an element in its standard state is zero and no need to take it into account.

Calculating involving the enthalpy change of reaction from enthalpy changes of formation

To determine the enthalpy change of reaction from enthalpy changes of formation, the corresponding elements of reactant and product should be considered. Firstly, write the balanced chemical equation for the standard enthalpy change of reaction at the top. The elements are written at the bottom with arrows pointing upwards and balanced the elements. The Hess's cycle of enthalpy change of a reaction is constructed as below.



By using Hess's law,
Route I = Route II
$\Delta H_1 + \Delta H_r = \Delta H_2$

For example, the following relevant data are given to determine the enthalpy change of reaction, the conversion of nitrogen oxide to nitrogen dioxide.

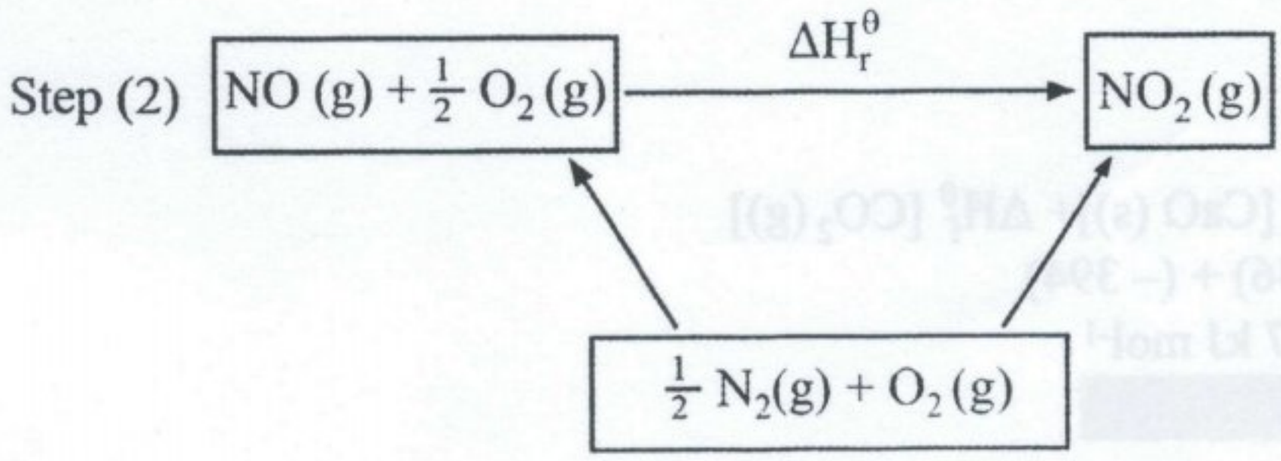
$\Delta H_f^\theta [NO\ (g)] = +90\ kJ\ mol^{-1}$

$\Delta H_f^\theta [NO_2\ (g)] = +33\ kJ\ mol^{-1}$

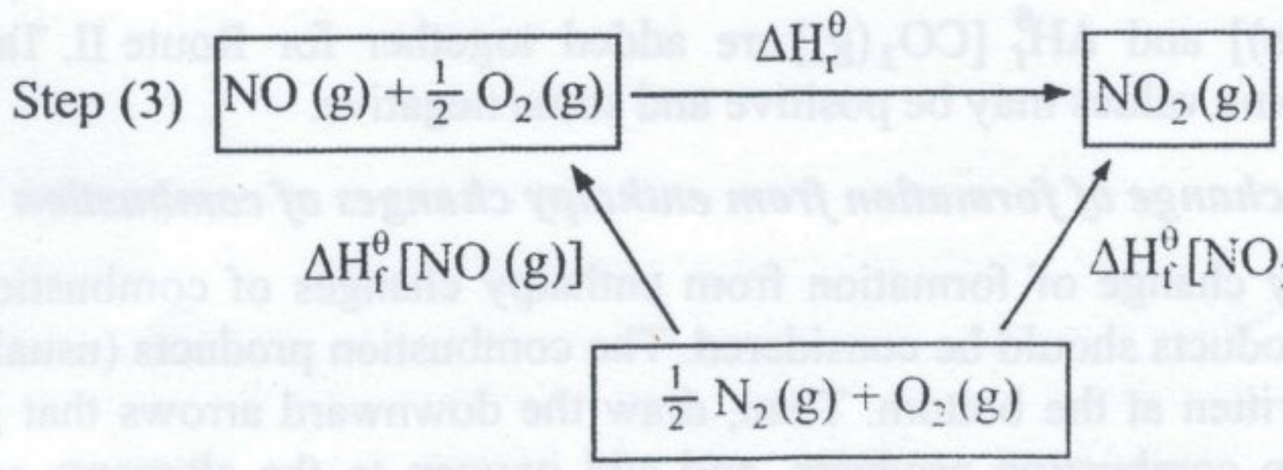
Construction of the enthalpy cycle for calculating the standard enthalpy change of reaction (ΔH_r^θ) is given below.

Step (1) $NO\ (g) + \frac{1}{2} O_2\ (g) \xrightarrow{\Delta H_r^\theta} NO_2\ (g)$

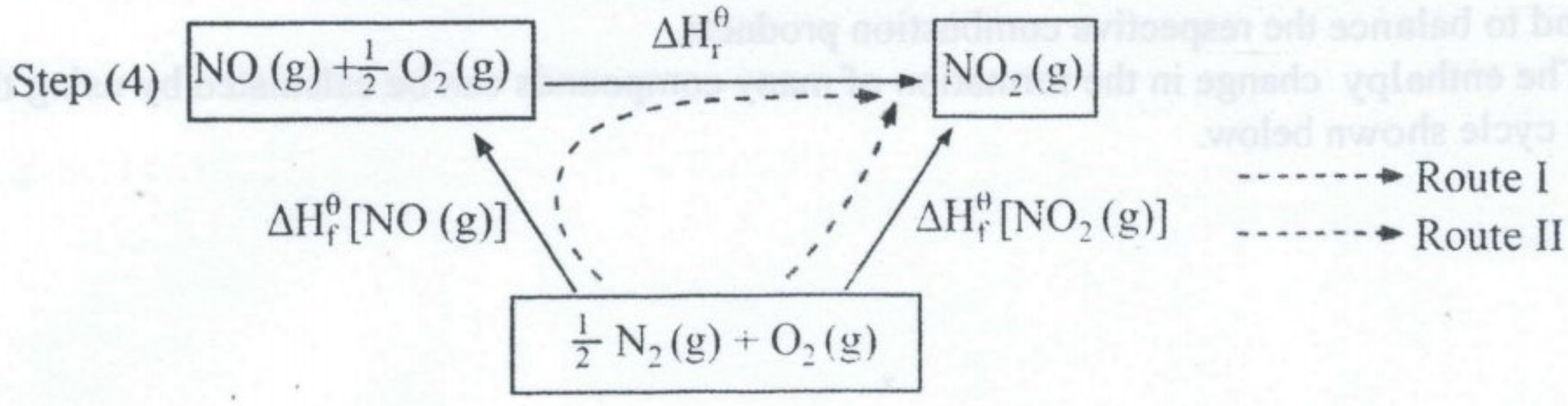
Step (2)



Step (3)



Step (4)



By using Hess's law,
Route I = Route II

$\Delta H_f^\theta [NO\ (g)] + \Delta H_r^\theta = \Delta H_f^\theta [NO_2\ (g)]$

$(+ 90) + \Delta H_r^0 = (+ 33)$

$\Delta H_r^\theta = - 57\ kJ\ mol^{-1}$

$\Delta H_r^\theta [NO\ (g)] = - 57\ kJ\ mol^{-1}$

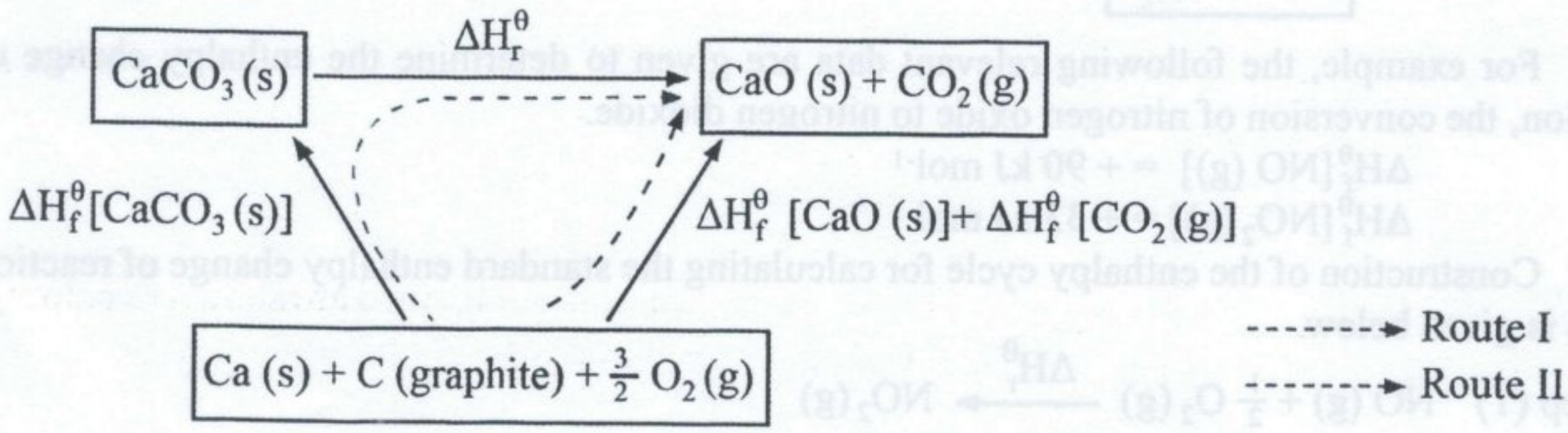
Example 5: Calculate the standard enthalpy change of the decomposition of calcium carbonate; $CaCO_3\ (s) \longrightarrow CaO\ (s) + CO_2\ (g)$ using the data given below.

$\Delta H_f^\theta [CaO\ (s)] = - 636\ kJ\ mol^{-1}$

$\Delta H_f^\theta [CO_2\ (g)] = - 394\ kJ\ mol^{-1}$

$\Delta H_f^\theta [CaCO_3\ (s)] = - 1207\ kJ\ mol^{-1}$

Solution:



By using Hess's law,
Route I = Route II

$\Delta H_f^\theta [CaCO_3\ (s)] + \Delta H_r^\theta = \Delta H_f^\theta [CaO\ (s)] + \Delta H_f^\theta [CO_2\ (g)]$

$(- 1207) + \Delta H_r^\theta = (- 636) + (- 394)$

$\Delta H_r^\theta = + 177\ kJ\ mol^{-1}$

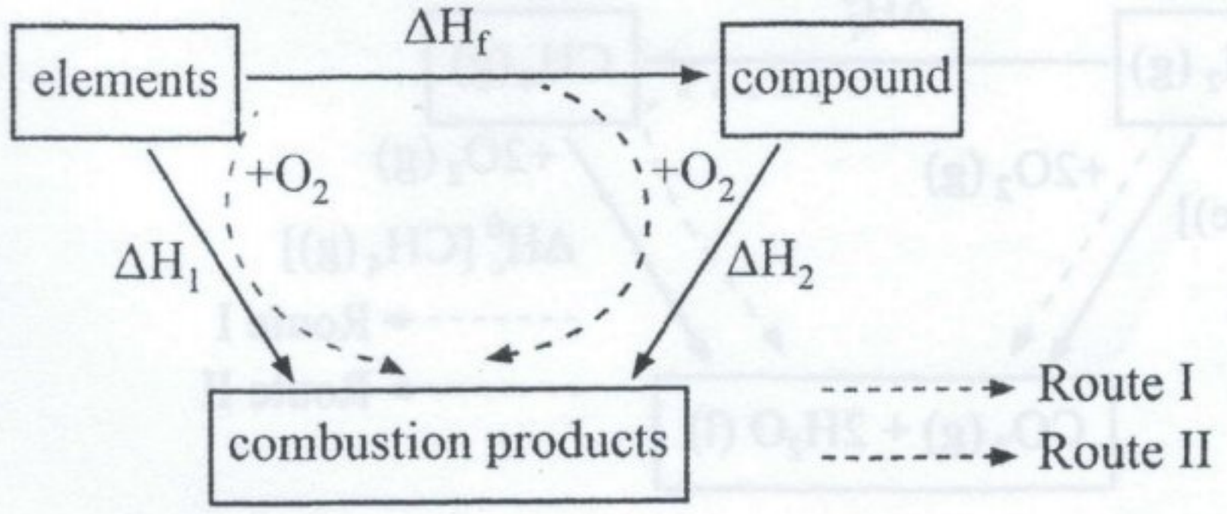
$\Delta H_r^0 [CaCO_3\ (s)] = + 177\ kJ\ mol^{-1}$

Note: The values for $\Delta H_f^\theta [CaO\ (s)]$ and $\Delta H_f^\theta [CO_2\ (g)]$ are added together for Route II. Take care to account for the fact that some values may be positive and some negative.

***Calculating** the enthalpy change of formation from enthalpy changes of combustion*

To determine the enthalpy change of formation from enthalpy changes of combustion, the corresponding combustion products should be considered. The combustion products (usually carbon dioxide and water) are written at the bottom. Then, draw the downward arrows that go from elements and compounds to combustion products, and add oxygen to the elements and compound to balance the respective combustion products.

The enthalpy change in the formation of many compounds can be calculated by using the enthalpy cycle shown below.



By using Hess's law,
Route I = Route II
$\Delta H_1 = \Delta H_f + \Delta H_2$

Consider the reaction for the formation of methane.

$$C\ (graphite) + 2H_2\ (g) \longrightarrow CH_4\ (g)$$

The standard enthalpy changes of combustion (ΔH_c^θ) for methane, carbon, and hydrogen are -

$\Delta H_c^\theta\ [CH_4\ (g)] = -\ 891\ kJ\ mol^{-1}$
$\Delta H_c^\theta\ [C\ (graphite)] = -\ 394\ kJ\ mol^{-1}$
$\Delta H_c^\theta\ [H_2\ (g)] = -\ 286\ kJ\ mol^{-1}$

The enthalpy cycle for calculating the standard enthalpy change for the formation of methane gas (ΔH_f^θ) is given below.

Step (1) $C\ (graphite) + 2H_2\ (g) \xrightarrow{\Delta H_f^\theta} CH_4\ (g)$

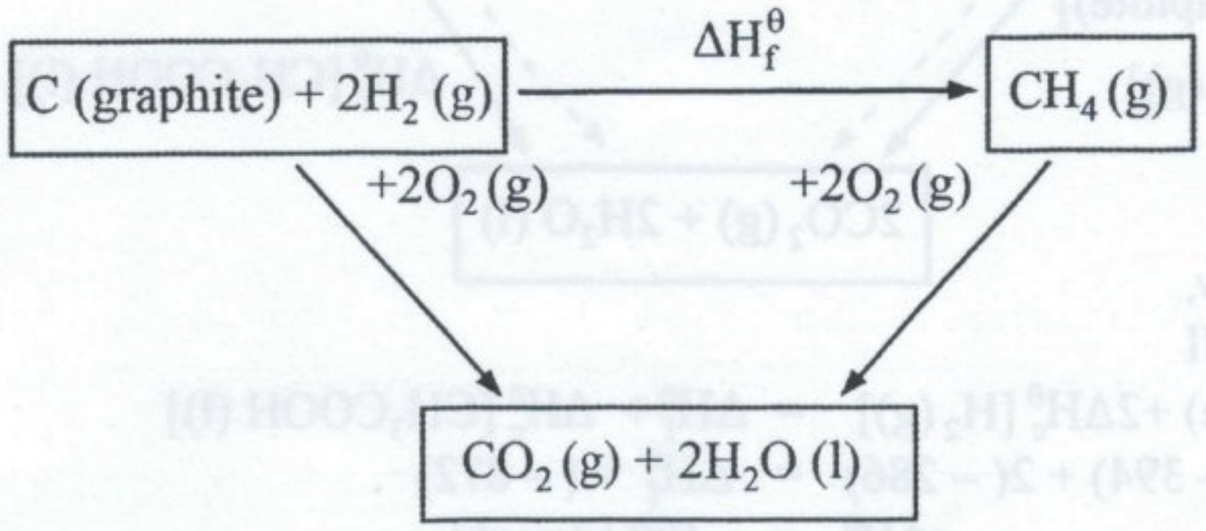
Step (2) The individual combustion reactions for elements and compound are shown as below.

$$C\ (graphite) + O_2\ (g) \longrightarrow CO_2\ (g)$$

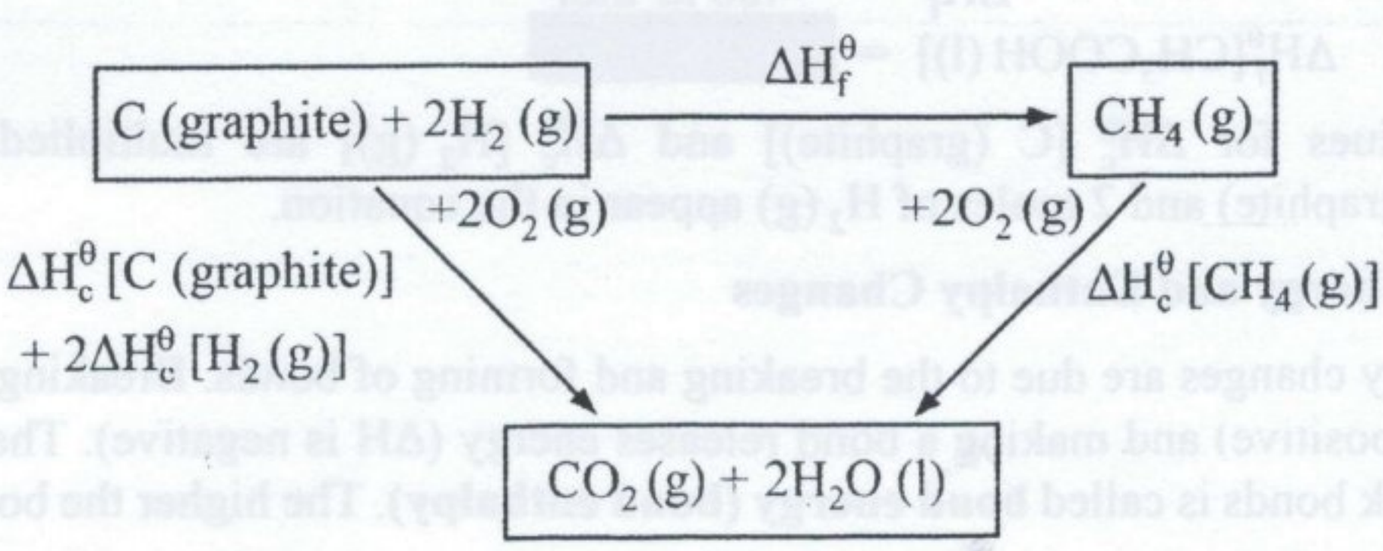
$$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \longrightarrow H_2O\ (l)$$

$$\therefore\ C\ (graphite) + 2H_2\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l)$$

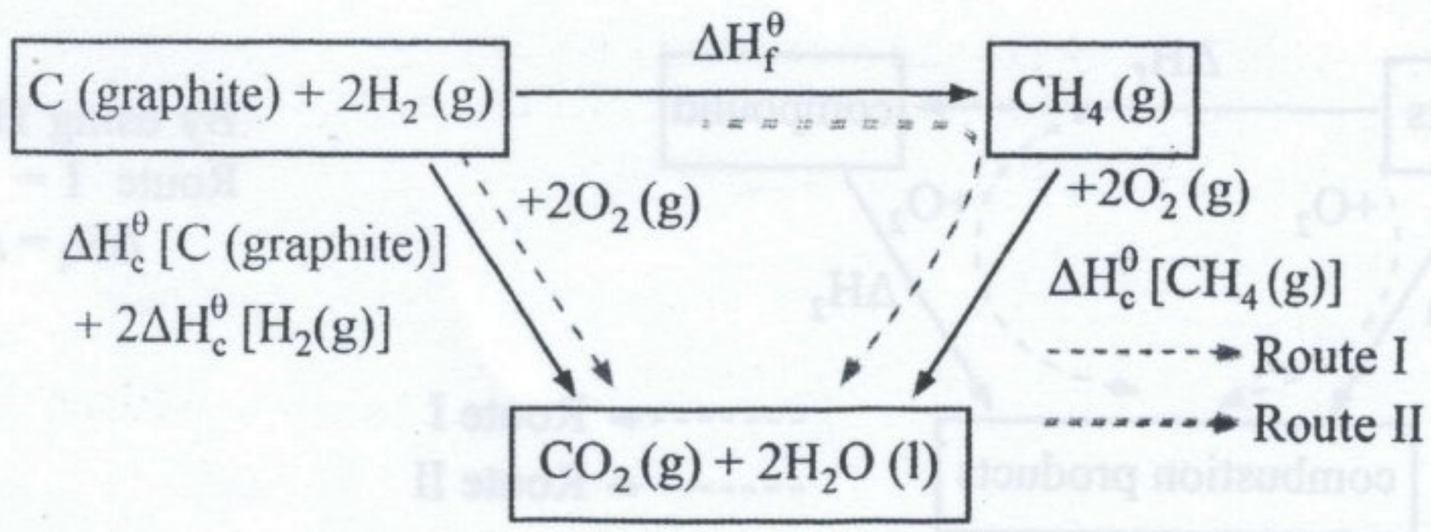
$$CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l)$$



Step (3)



Step (4)



By using Hess's law,

Route I = Route II

$\Delta H_c^\theta [C(graphite)] + 2\Delta H_c^\theta [H_2(g)] = \Delta H_f^\theta + \Delta H_c^\theta [CH_4(g)]$

$(-394) + 2(-286) = \Delta H_f^0 + (-891)$

$\Delta H_f^0 = -75 \text{ kJ mol}^{-1}$

$\therefore \Delta H_f^\theta [CH_4(g)] = -75 \text{ kJ mol}^{-1}$

Note: The value for $\Delta H_c^\theta [H_2(g)]$ is multiplied by 2 because 2 moles of H_2 (g) appear in the equation.

Example 6: Calculate the standard enthalpy change of formation of ethanoic acid, CH_3COOH.

$2C \text{ (graphite)} + 2H_2(g) + O_2(g) \longrightarrow CH_3COOH(l)$

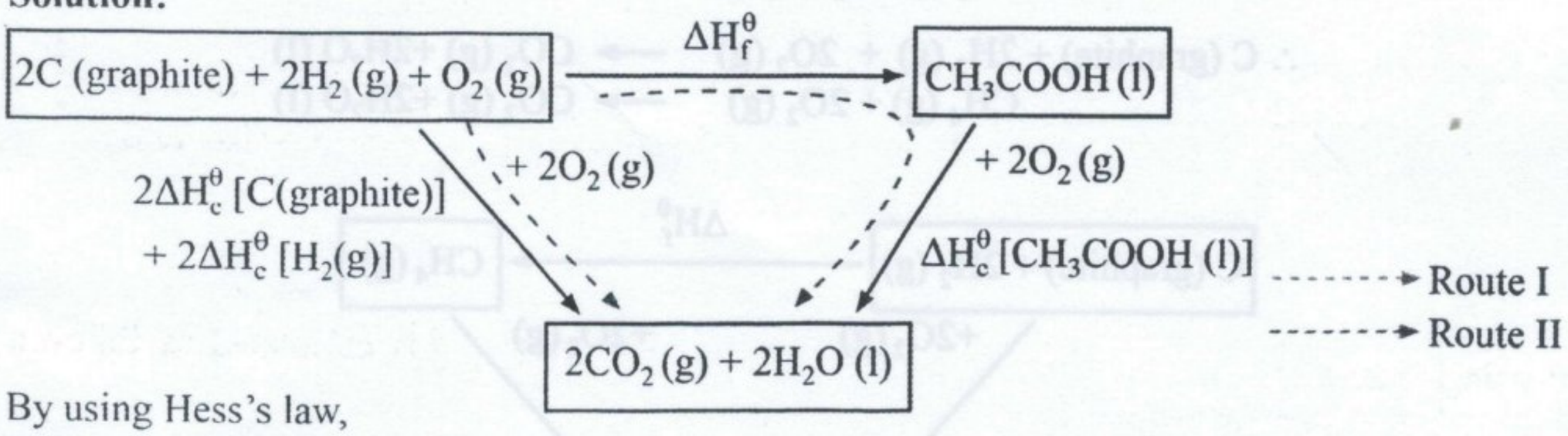
The relevant enthalpy changes of combustions are given below.

$\Delta H_c^\theta [C \text{ (graphite)}] = -394 \text{ kJ mol}^{-1}$

$\Delta H_c^\theta [H_2(g)] = -286 \text{ kJ mol}^{-1}$

$\Delta H_c^\theta [CH_3COOH(l)] = -872 \text{ kJ mol}^{-1}$

Solution:



By using Hess's law,

Route I = Route II

$2\Delta H_c^\theta [C \text{ (graphite)} + 2\Delta H_c^\theta [H_2(g)] = \Delta H_f^0 + \Delta H_c^0 [CH_3COOH(l)]$

$2(-394) + 2(-286) = \Delta H_f^\theta + (-872)$

$\Delta H_f^\theta = -488 \text{ kJ mol}^{-1}$

$\Delta H_f^\theta [CH_3COOH(l)] = -488 \text{ kJ mol}^{-1}$

Note: The values for $\Delta H_c^\theta [C \text{ (graphite)}]$ and $\Delta H_c^\theta [H_2(g)]$ are multiplied by 2 because 2 moles of C (graphite) and 2 moles of H_2 (g) appear in the equation.

(b) Bond Energy and Enthalpy Changes

Enthalpy changes are due to the breaking and forming of bonds. Breaking a bond absorbs energy (ΔH is positive) and making a bond releases energy (ΔH is negative). The energy needed to make or break bonds is called **bond energy (bond enthalpy)**. The higher the bond enthalpy, the

more energy needed to break the bond, and the stronger is the bond.The symbol for bond enthalpy is **E**. So, E(C–H) refers to the bond enthalpy of a mole of single bonds between carbon and hydrogen atoms. The bond enthalpy for double and triple bonds refers to a mole of double or triple bonds.

When new bonds are formed the amount of energy released is the same as the amount of energy absorbed when the same type of bond is broken. For example, the bond enthalpies for the breaking and forming bonds of bromine molecules are + 193 kJ mol^{-1} and – 193 kJ mol^{-1}, respectively.

$Br_2\,(g) \longrightarrow 2Br\,(g)$ E(Br–Br) = + 193 kJ mol^{-1}
$2Br\,(g) \longrightarrow Br_2\,(g)$ E(Br–Br) = – 193 kJ mol^{-1}

Hess's law can also be used to find approximate values of enthalpy change of a reaction using bond enthalpies.

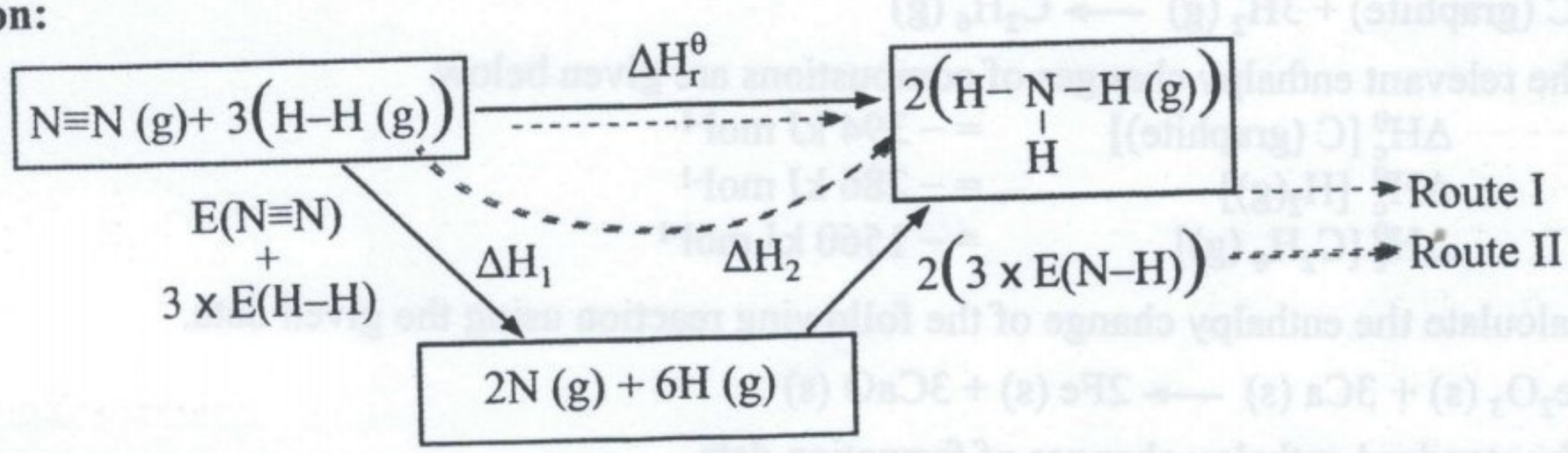
The bond enthalpy can be used to calculate the enthalpy change of a reaction that cannot be measured directly.

Example 7: Calculate the standard enthalpy change of reaction of Haber process by using the Hess's cycle from the data given below.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

The relevant bond enthalpies are E(N≡N) = 945 kJ mol^{-1}, E(H–H) = 436 kJ mol^{-1}, and E(N–H) = 391 kJ mol^{-1}

Solution:



By using Hess's law, the standard enthalpy change of reaction, ΔH_r^θ is calculated as follows:

Route I = Route II

$\Delta H_r^\theta = \Delta H_1 + \Delta H_2$

ΔH_r^θ = enthalpy change for bonds broken + enthalpy change for bonds formed

$= [E(N\equiv N) + 3 \times E(H–H)] + 2\,[3 \times (–E(N–H)]$

$= 945 + 3(436) + 6\,(–391)$

$\Delta H_r^\theta = 2253 + (– 2346) =$ – 93 kJ mol^{-1}

Calculating the enthalpy change without using the enthalpy cycle

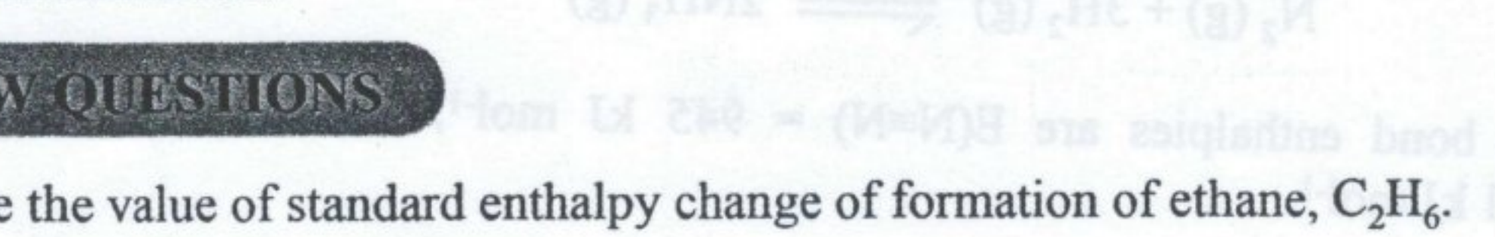
Example 8: Calculate the enthalpy change of the combustion (ΔH_c) of ethanol from given bond enthalpy values.

$$C_2H_5OH\,(l) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 3H_2O\,(l)$$

E(C–C) = + 347 kJ mol^{-1}, E(C–H) = + 410 kJ mol^{-1}, E(C–O) = + 336 kJ mol^{-1},
E(O=O) = + 496 kJ mol^{-1}, E(C=O) = + 805 kJ mol^{-1}, E(O–H) = + 465 kJ mol^{-1}

Solution:

$$C_2H_5OH\,(l) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 3H_2O\,(l)$$



ΔH for bonds broken $= E(C–C) + 5(E(C–H)) + E(C–O) + E(O–H) + 3(E(O=O))$
$= 347 + 5(410) + (336) + (465) + 3(496)$
$= +4686\ kJ\ mol^{-1}$

ΔH for bonds formed $= 2[2 \times (-E(C=O))] + 3[2 \times (-E(O–H))]$
$= -4(805) + -6(465)$
$= -6010\ kJ\ mol^{-1}$

ΔH_c = enthalpy change for bonds broken + enthalpy change for bonds formed
$= (+4686) + (-6010)$
$\therefore \Delta H_c =$ **– 1324 kJ mol^{-1}**

REVIEW QUESTIONS

(1) Calculate the value of standard enthalpy change of formation of ethane, C_2H_6.

$2C\,(graphite) + 3H_2\,(g) \longrightarrow C_2H_6\,(g)$

The relevant enthalpy changes of combustions are given below.

$\Delta H_c^{\theta}\,[C\,(graphite)] = -394\ kJ\ mol^{-1}$
$\Delta H_c^{0}\,[H_2(g)] = -286\ kJ\ mol^{-1}$
$\Delta H_c^{0}\,[C_2H_6\,(g)] = -1560\ kJ\ mol^{-1}$

(2) Calculate the enthalpy change of the following reaction using the given data.

$Fe_2O_3\,(s) + 3Ca\,(s) \longrightarrow 2Fe\,(s) + 3CaO\,(s)$

The standard enthalpy changes of formation data

Fe_2O_3 (s)	Ca (s)	Fe (s)	CaO (s)
– 824 kJ mol^{-1}	0 kJ mol^{-1}	0 kJ mol^{-1}	– 636 kJ mol^{-1}

(3) Using the bond enthalpy values, calculate the enthalpy change for the combustion of methane shown by the equation $CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l)$

$E(C–H) = 410\ kJ\ mol^{-1}$, $E(O=O) = 496\ kJ\ mol^{-1}$, $E(C=O) = 805\ kJ\ mol^{-1}$,
$E(O–H) = 465\ kJ\ mol^{-1}$

Key Term

- **Bond energy (Bond enthalpy)** is the amount of energy required in bond breaking or making of one mole of chemical bonds in a molecular element or compound.

Chemistry in Society

- In burning fuels (such as paraffin, coal, propane, and butane) the exothermic reaction takes place during the reaction.
- The endothermic reaction takes place during cooking food, baking bread, boiling water, and warming the food.
- A lot of weight loss applications use Hess's law concept to calculate the number of calories burned during a workout.
- Hand warmers produce heat from the exothermic reaction and Hess's law can help to find out the total change in enthalpy and deduce how many amounts of each ingredient are needed to keep warm for hours.
- For the most effective energy choice, the industries such as automobile manufacturers must determine how much energy the engine consumes or generates while burning fuels by using Hess's law.

EXERCISES

Q 1 to Q 4 (Remembering and Understanding)

1. State TRUE or FALSE for each of the following statements. If FALSE, correct it.

   (a) Energy is released in all chemical reactions.
   (b) In an exothermic reaction, the surrounding temperature is increased.
   (c) An endothermic process may be used as a cooling system.
   (d) Total enthalpy change for a chemical reaction is dependent on the route by which the reaction takes place.
   (e) The neutralisation reaction is endothermic and the enthalpy change is positive.

2. Select the correct word or words given in the brackets.

   (a) The enthalpy change of (neutralisation, solution, formation) is the heat change that occours when one mole of a substance is dissolved in water.
   (b) The bond breaking is a/an (exothermic, endothermic, heat evolving) process.
   (c) Standard enthalpy change is measured at (0 °C, 273 K, 25 °C), and 760 mmHg.
   (d) Combustion of fuels is a/an (exothermic, endothermic, heat absorbing) process.
   (e) When the energy needed to break bonds is (less than, greater than, equal to) the energy needed to form bonds, the reaction is exothermic.

3. Fill in the blanks with a suitable word or phrase.

   (a) A process in which the system absorbs heat from its surroundings is called _____.
   (b) The symbol of the standard enthalpy change is _____.
   (c) Heat liberated by a chemical reaction is assigned by _____.
   (d) Change in enthalpy of a system is due to the heat supplied at a constant _____.
   (e) The highly accurate values of enthalpy changes of combustion can be measured by using a special apparatus called _____.

4. Is each of the following reactions endothermic or exothermic? Give a reason for your answer.
   (a) $C\ (graphite) + H_2O\ (g) \longrightarrow CO\ (g) + H_2\ (g)$ $\quad \Delta H = (+)$
   (b) $CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l)$ $\quad \Delta H = (-)$
   (c) $H_2\ (g) + I_2\ (g) \longrightarrow 2HI\ (g) + 21.0\ kJ$
   (d) making of a chemical bond
   (e) $\frac{1}{2} N_2\ (g) + \frac{1}{2} O_2\ (g) + heat \longrightarrow NO\ (g)$

Q 5 to Q 10 (Analysing and Problem Solving)

5. (a) The energy from burning 0.45 g of propane was transferred to 100 cm^3 of water to raise its temperature by 20 °C. Calculate the enthalpy change (in kJ). (Assume that 1cm^3 of water has a mass of 1 g, the specific heat capacity of water is 4.18 J g^{-1} $°C^{-1}$.)
   (b) The enthalpy of combustion of ethanol is –1367 kJ mol^{-1}. Using this value, calculate the number of moles of ethanol required to raise the temperature of 500 g of water from 18 °C to 100 °C. (C = 12, O = 16, H =1) (c = 4.18 J g^{-1} $°C^{-1}$)

6. (a) When 8.0 g of sodium chloride is dissolved in 40 cm^3 of water the temperature falls to 20.5 °C from 22.0 °C. Calculate the energy absorbed by the solution when sodium chloride dissolves. Answer with three significant figures. (c = 4.18 J g^{-1} $°C^{-1}$)
   (b) A 75 cm^3 of 2.0 mol dm^{-3} ethanoic acid, CH_3COOH, was placed in a styrofoam cup. The temperature was 18.2 °C. A 75 cm^3 of 2.0 mol dm^{-3} ammonium hydroxide, NH_4OH temperature was 18.6 °C. After mixing these two solutions, the highest temperature was 31.0 °C. Calculate ΔH for the neutralisation. (c = 4.18 J g^{-1} $°C^{-1}$)

7. (a) Write a balanced chemical equation corresponding to the standard enthalpy change of combustion of the following:
   (i) carbon (graphite) (ii) $H_2\ (g)$ (iii) $N_2\ (g)$ (iv) S (s) (v) Mg (g)
   (b) Write a balanced chemical equation corresponding to the standard enthalpy change of formation of the following compounds.
   (i) NaCl (s) (ii) $H_2SO_4\ (l)$ (iii) $NaHCO_3\ (s)$ (iv) $MgCO_3\ (s)$ (v) HCl (g)

8. (a) Calculate the standard enthalpy of formation of butane gas, C_4H_{10}, from the following data:
   enthalpy of combustion of graphite = – 394 kJ mol^{-1},
   enthalpy of combustion of hydrogen = – 286 kJ mol^{-1}
   enthalpy of combustion of butane = – 2877 kJ mol^{-1}
   (b) Calculate the enthalpy change of the following reaction:
   $CO\ (g) + 2H_2\ (g) \longrightarrow CH_3OH\ (g)$
   The relevant enthalpy changes in combustion data are given below.
   enthalpy of combustion of CO (g) = – 283 kJ mol^{-1}
   enthalpy of combustion of H_2 (g) = – 286 kJ mol^{-1}
   enthalpy of combustion of CH_3OH (g) = – 726 kJ mol^{-1}

9. Draw the enthalpy cycle to calculate ΔH_r^θ for the reaction;
   $Al_2O_3\ (s) + 3Mg\ (s) \longrightarrow 3MgO\ (s) + 2Al\ (s)$
   Calculate the ΔH_r^θ using the following data:
   ΔH_f^θ $[Al_2O_3\ (s)]$ = – 1676 kJ mol^{-1}
   ΔH_f^θ [MgO (s)] = – 602 kJ mol^{-1}

10. Draw the enthalpy cycle and calculate ΔH_r^θ for the reaction from the given data.

$2Al\,(s) + Fe_2O_3\,(s) \longrightarrow 2Fe\,(s) + Al_2O_3\,(s)$

$\Delta H_f^\theta\,[Fe_2O_3\,(s)] = -824\ kJ\ mol^{-1}$

$\Delta H_f^\theta\,[Al_2O_3\,(s)] = -1676\ kJ\ mol^{-1}$

Q 11 and Q 14 (Critical Thinking)

11. Draw the energy level diagrams for the following reactions and identify exothermic or endothermic.

(a) $Fe\,(s) + S\,(s) \longrightarrow FeS(s)$ $\Delta H = -110\ kJ\ mol^{-1}$

(b) $CaCO_3\,(s) \longrightarrow CaO\,(s) + CO_2\,(g)$ $\Delta H = +178\ kJ\ mol^{-1}$

12. Using the enthalpies of combustion given in the following table, which organic compound releases the greatest amount of energy per gram during combustion? (C = 12, H = 1, O = 16)

Fuel	ΔH_c (kJ mol^{-1})
methanol	− 726
ethanol	− 1367
n-octane	− 5471

13. (a) (i) Explain what is meant by the H–I bond energy. (ii) Write the symbol for H–I bond energy. (iii) Write a hypothetical equation that shows the change brought about in determining the H–I bond energy.

(b) Hydrogen chloride can react with acetylene (ethyne) in a two-stage addition process to give a saturated product as follows:

$C_2H_2\,(g) + 2HCl\,(g) \longrightarrow C_2H_4Cl_2\,(g)$

Calculate the enthalpy change of this reaction using the following bond enthalpy data.
$E(C{\equiv}C) = 835\ kJ\ mol^{-1}$, $E(C–H) = 410\ kJ\ mol^{-1}$, $E(C–C) = 347\ kJ\ mol^{-1}$
$E(C–Cl) = 326\ kJ\ mol^{-1}$, $E(H–Cl) = 428\ kJ\ mol^{-1}$

14. The compound diborane (B_2H_6) is used as rocket fuel. The combustion of diborane is shown in the following equation:

$B_2H_6\,(g) + 3O_2\,(g) \longrightarrow B_2O_3\,(s) + 3H_2O\,(l)$

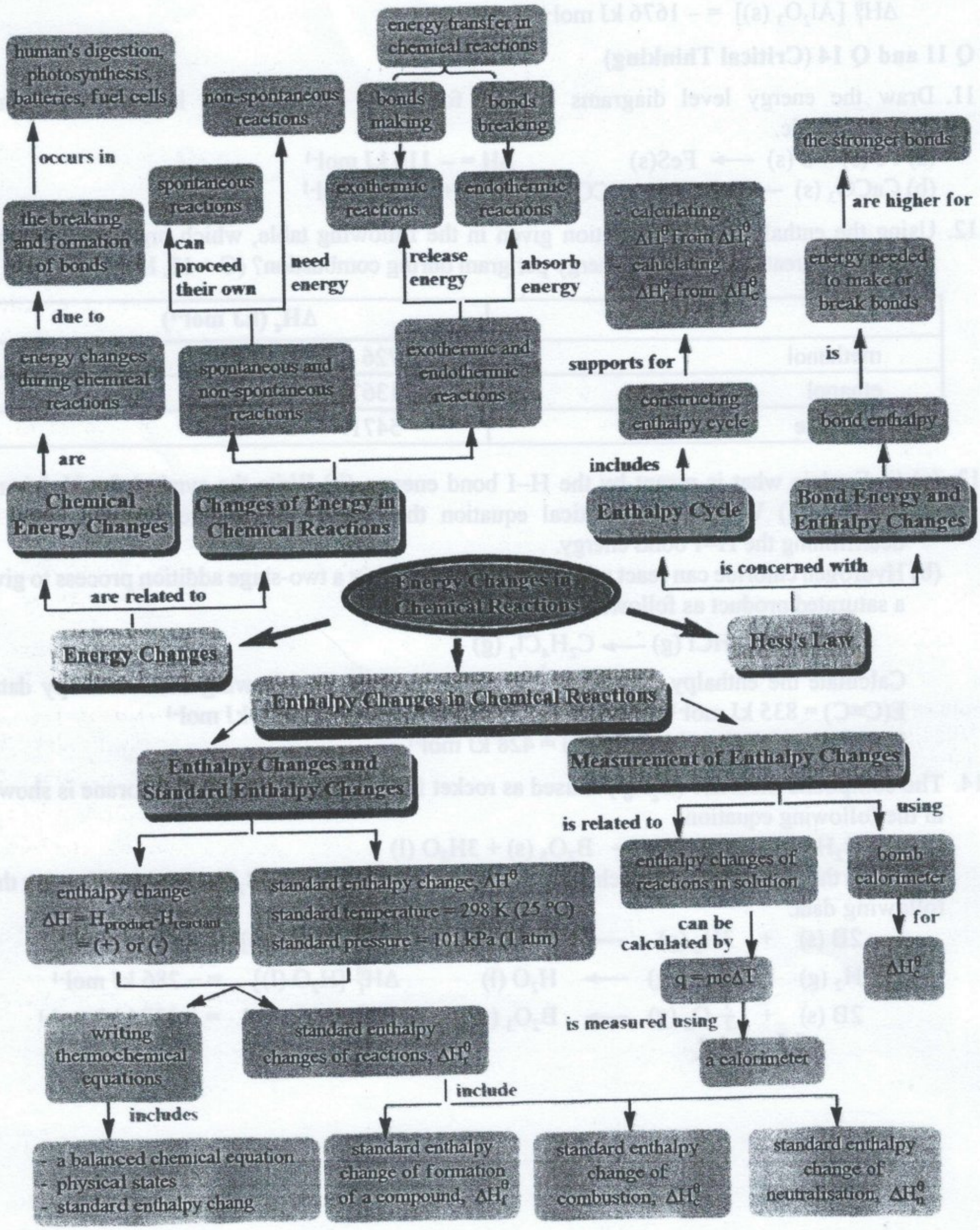
Calculate the standard enthalpy change of combustion of diborane (B_2H_6) in kJ mol^{-1}, using the following data:

$2B\,(s) + 3H_2\,(g) \longrightarrow B_2H_6\,(g)$ $\Delta H_f^\theta\,[B_2H_6\,(g)] = -36\ kJ\ mol^{-1}$

$H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l)$ $\Delta H_f^\theta\,[H_2O\,(l)] = -286\ kJ\ mol^{-1}$

$2B\,(s) + \frac{3}{2}O_2\,(g) \longrightarrow B_2O_3\,(s)$ $\Delta H_f^\theta\,[B_2O_3\,(s)] = -1274\ kJ\ mol^{-1}$

CHAPTER REVIEW
(Concept Map)



CHAPTER 3

CHEMICAL KINETICS: RATES OF REACTION

Previously, we learned how to write chemical equations to express chemical reactions and then use these equations to calculate the amounts of products produced and reactants consumed in such reactions. Every reaction has a rate, or speed, at which it proceeds. Different chemical reactions occur at different rates (speeds). Some are fast and some are very slow. For example, an explosion of dynamite, striking of a match, and burning of magnesium ribbon take within a second, whereas weathering of rocks and rusting of an iron pipe happen for years. Chemical reactions occur all around us, crucially important in environmental, biological, and industrial processes. For instance, depletion of the ozone layer depends on the relative rates of reactions that produce and destroy ozone molecules; enzyme action is essential in food preservatives; the economical synthesis of ammonia to produce fertiliser depends on the rate at which gaseous nitrogen and hydrogen can be converted to ammonia. Hence, knowledge of reaction rates is required in drug design, pollution control, and food processing. The study of reaction rates is known as "chemical kinetics". In this chapter, the rate of reaction that is central to the understanding of chemical reactions will be focused.

Explosion of dynamite (within a second)

Spoiling of preserved food (weeks, months)

Rusting of an iron pipe (months, years)

Weathering of rocks (very slow for years)

Learning Outcomes

After completing this chapter, students will be able to:

- express the rate of a chemical reaction in terms of change in concentration of reactants and products;
- determine the rate of reaction;
- explain the important role of collision theory;
- define the term activation energy;
- describe the effects of changes in concentration of reactants, particle size of reactants, pressure of gases, temperature and light on the rate of a reaction;
- differentiate the catalytic effects of positive, negative, homogeneous, heterogeneous catalysts and biocatalysts.

3.1 REACTION RATES

Rate is a measure of how fast or how slow the reaction is. To describe the quantitative measurement of a reaction rate, it is necessary to specify how fast the reactants are used up or the products are formed.

An iron nail reacts slowly in the air as it rusts. White phosphorus bursts into flames when exposed to air. Candle wax burns only after the wick of the candle is lighted. These reactions with the oxygen in the air take place at different rates. The rate of reaction varies greatly for different reactions and under different conditions. The rate of reaction means measuring the change in the amount of a product produced or a reactant used up in the time taken for that change. In other words, the reaction rate is usually expressed as the change in the amount of a reactant used up or the product formed in a unit of time.

For the progress of a simple reaction (Reactant A→Product B), the rate of this reaction can be illustrated as shown in Figure 3.1.

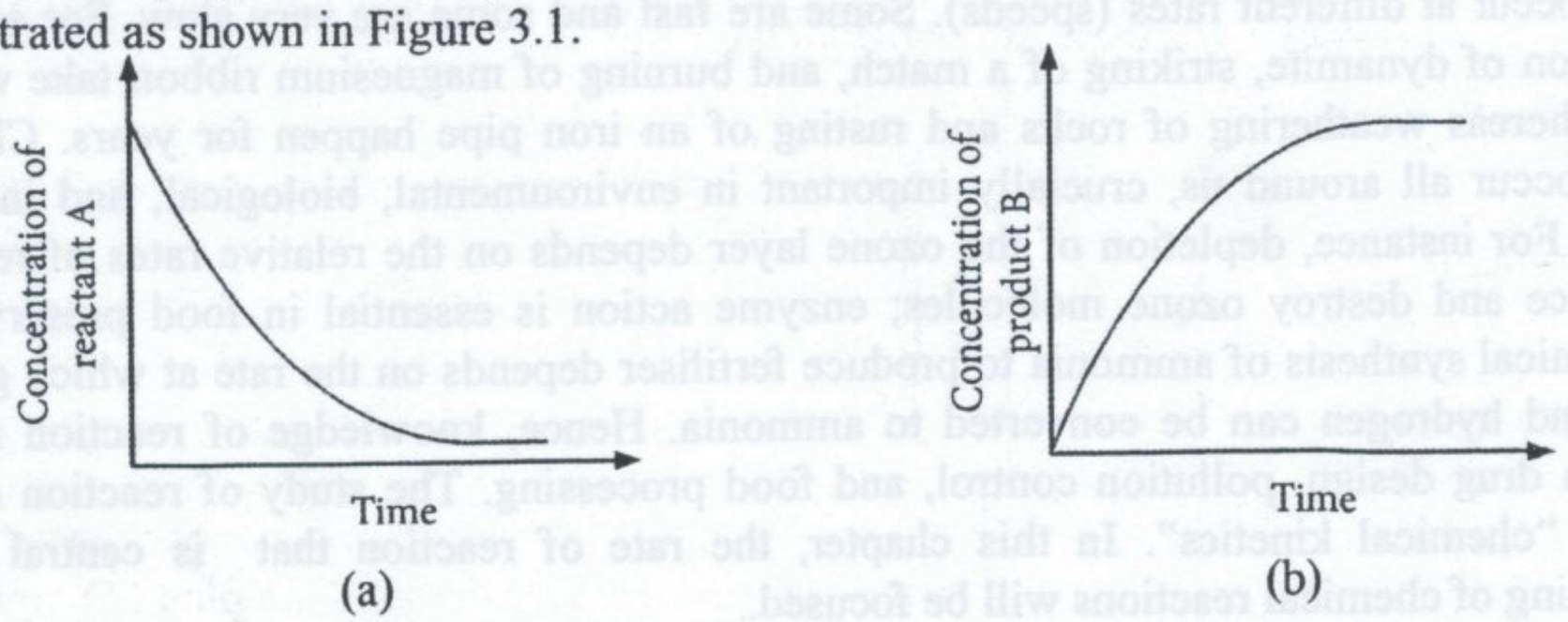


Figure 3.1 Plots Showing Rate of Reaction in Terms of (a) Decrease in Concentration of Reactant A (b) Increase in Concentration of Product B with Time

Consider, as an example, the reaction between magnesium ribbon and hydrochloric acid. Magnesium reacts with dilute hydrochloric acid giving off hydrogen gas according to the following chemical equation:

$$Mg\,(s) + 2HCl\,(aq) \longrightarrow MgCl_2\,(aq) + H_2\,(g)$$

This reaction can be readily observed in how long it takes before there is no magnesium left in the flask. In other words, the reactants have been used up. Alternatively, how quickly the hydrogen gas evolved during the reaction. The volume of hydrogen gas released in the process of reaction at time intervals can be measured as shown in Figure 3.2.

The rate of reaction (in terms of the reactant) is expressed as

$$\text{rate of disappearance of Mg} = \frac{\text{mass of Mg reacted}}{\text{time}}$$

Similarly, the rate of reaction (in terms of the product) is expressed as

$$\text{rate of formation of } H_2 = \frac{\text{volume of } H_2 \text{ collected}}{\text{time}}$$

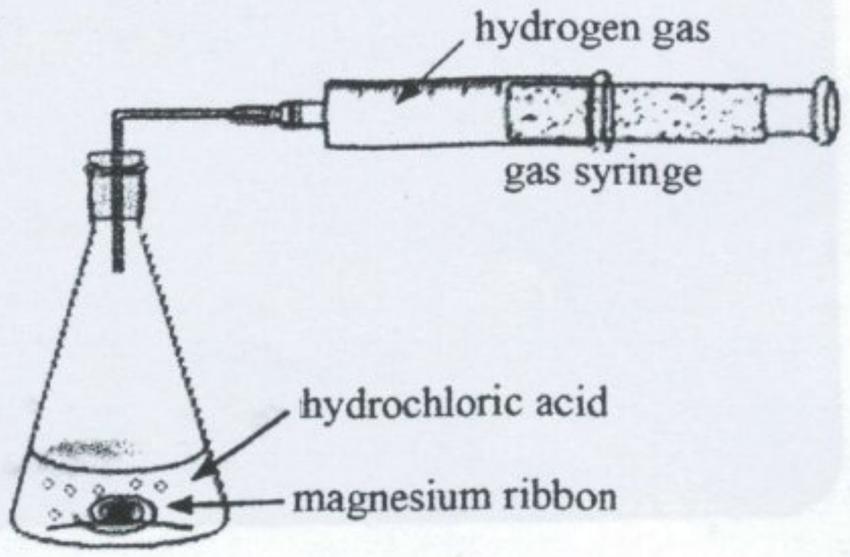


Figure 3.2 Measuring the Volume of Hydrogen Gas Released with Time by Gas Syringe Method

Thus, the rate of a reaction can be expressed as the change in the amount (mass, volume or concentration) of reactants or products per unit of time.

$$\text{rate} = \frac{\text{change in the amount (mass, volume, or concentration) of reactants or products}}{\text{time taken for this change}}$$

If the substance is a gas, the amount consumed or formed is expressed in pressure units or as measured in volume. Concentration units are used if the reactant or product is in solution. The time measurement is expressed in whatever units fit the reaction (seconds, minutes, hours, days, months or years).

Generally, in chemical reactions, the **rate of a reaction** in solution is measured in terms of a decrease in the concentration of the reactant or an increase in the concentration of the product per unit time at a constant temperature.

$$\text{rate} = \frac{\text{change in concentration}}{\text{change in time}} = \frac{\text{concentration at time } t_2 - \text{concentration at time } t_1}{t_2 - t_1}$$

$$\text{rate of reactant used up} = -\frac{\Delta[\text{reactant}]}{\Delta t}$$

$$\text{rate of product formed} = +\frac{\Delta[\text{product}]}{\Delta t}$$

where the delta (Δ) means change and the square bracket [ ] represents molar concentration. The minus (–) sign means a decrease in the concentration of the reactant. The plus (+) sign means an increase in the concentration of the product. Rate is expressed as a positive quantity.

For a general chemical reaction $aA + bB \xrightarrow{k} cC + dD$

where a, b, c, and d are the stoichiometric coefficients of the reactants and products in the balanced chemical equation, and *k* is the rate constant, which explains the relationship between the molar concentration of the reactants and the rate of a chemical reaction.

Thus, the rate for the reaction is $\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$

The mole ratios from the balanced chemical equation can be used to determine the rates of change in concentrations of products and reactants. The rate of reaction can then be derived from any one of these individual rates.

Example 1: When the following reaction of zinc and dilute hydrochloric acid takes place, 30 g of zinc has been used up after 2 min. Calculate the rate of the reaction in terms of the mole per second. (Zn = 65.38)

$$Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

Solution: $\text{moles of zinc} = 30\text{ g} \times \frac{1\text{ mol}}{65.38\text{ g}} = 0.46\text{ mol}$

reaction time (in seconds) $t = 2 \times 60 = 120\text{ s}$

$$\text{rate} = \frac{\text{moles of zinc used}}{\text{time}} = \frac{0.46\text{ mol}}{120\text{ s}} = 0.004\text{ mol s}^{-1}$$

The rate of reaction is 0.004 mol s^{-1}.

Example 2: Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products.

(a) $C_6H_{12}O_6\,(s) \longrightarrow 2C_2H_5OH\,(aq) + 2CO_2\,(g)$ (b) $3O_2\,(g) \longrightarrow 2O_3\,(g)$

Solution: (a) rate $= -\frac{\Delta[C_6H_{12}O_6]}{\Delta t} = \frac{1}{2}\frac{\Delta[C_2H_5OH]}{\Delta t} = \frac{1}{2}\frac{\Delta[CO_2]}{\Delta t}$

(b) rate $= \frac{1}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[O_3]}{\Delta t}$

Example 3: If the concentration of H_2 is 0.674 mol dm^{-3} at time t_1 = 1 s and 0.526 mol dm^{-3} at time t_2 = 2 s after the reaction begins, calculate the rate of the following reaction:

$$H_2\,(g) + 2ICl\,(g) \longrightarrow I_2\,(g) + 2HCl\,(g)$$

Solution: $\text{rate} = -\frac{\Delta[H_2]}{\Delta t}$

$$= -\frac{0.526\ \text{mol dm}^{-3} - 0.674\ \text{mol dm}^{-3}}{(2\ \text{s} - 1\text{s})} = -\frac{-0.148\ \text{mol dm}^{-3}}{1\ \text{s}} = 0.148\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

The rate of the reaction is 0.148 mol dm^{-3} s^{-1}

Example 4: In the reaction 2A (aq) $\longrightarrow$ 4B (aq) + C (aq), the decomposition of compound A at 300 K in a solution with constant volume can be followed by monitoring the concentration of A. Initially (at t = 0), the concentration of A is 2.00 mol dm^{-3}, and after 120 s, it is reduced to 1.76 mol dm^{-3}. Calculate the rate of the reaction.

Solution: $\Delta[A] = [A]_t - [A]_0 = (1.76 - 2.00)\ \text{mol dm}^{-3} = -0.24\ \text{mol dm}^{-3}$

$$\text{rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = -\frac{1}{2} \times \left(\frac{-0.24\ \text{mol dm}^{-3}}{120\ \text{s}}\right) = 1.0 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

The rate of the reaction is 1.0×10^{-3} mol dm^{-3} s^{-1}.

REVIEW QUESTIONS

(1) (a) (i) What is the expression for the rate of a reaction?
(ii) What are the units of the rate of a reaction?
(b) Give two examples each for slow and fast reactions.

(2) (a) Consider the following processes and categorise whether it takes time in seconds, minutes, hours, days, months, or years: the rusting of the iron door, a reaction between sodium and water, the processing of grape wine, the decay of buildings and cars by acid rain, the burning of magnesium ribbon.
(b) Choose the correct units to measure the rate at which (i) magnesium is used up (ii) carbon dioxide is given off (iii) sulphur is formed (iv) concentration of hydrogen chloride is changed in their respective reactions.
$dm^3\ min^{-1}$, $g\ s^{-1}$, $mol\ dm^{-3}\ s^{-1}$

(3) Write the rate expression for each of the following reactions:
(a) $Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$
(b) $2N_2O_5\,(g) \longrightarrow 4NO_2\,(g) + O_2\,(g)$

Key Term

- **Rate of a reaction** is measured in terms of the change in amount of a reactant or a product per unit of time.

3.2 COLLISION THEORY AND ACTIVATION ENERGY

A number of variables mentioned in Section 3.3 affect the rate of a reaction. To understand why these variables affect reaction rates, the conditions that are necessary for a reaction to take place should be considered. Collision theory explains how chemical reactions occur. It is based on the kinetic molecular theory of gases. Reactant particles moving in random directions possess kinetic energy. When they frequently collide with one another, the energy is transferred as a result of the collision. Not all collisions between reactant particles result in the formation of reaction products. For a reaction to occur, colliding particles must impact with certain minimum energy known as an activation energy. This section describes the required conditions of how reactions occur.

(a) Collision Theory

Collision orientation and sufficient energy

For a reaction to take place, reactant particles or molecules must be moving and colliding with each other. During a collision, the spatial orientation of the reactant molecules is important to determine whether or not a reaction occurs. If the colliding particles have the incorrect orientation, they will bounce off each other. The unsuccessful collisions with insufficient energy do not produce a reaction. When the particles collide with the correct orientation, they must have enough energy for a **successful collision** (effective collision) to produce a reaction (Figure 3.3).

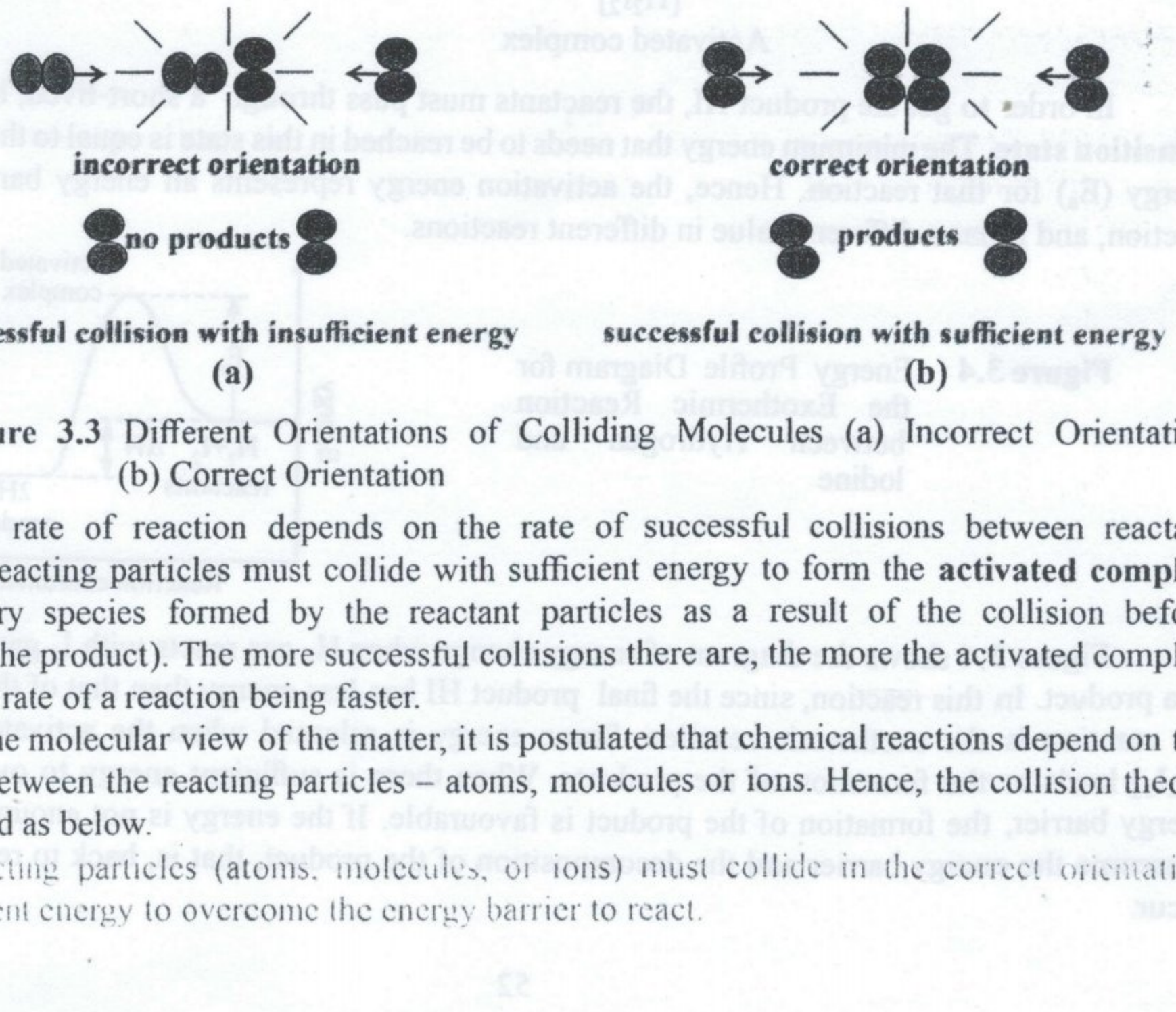


Figure 3.3 Different Orientations of Colliding Molecules (a) Incorrect Orientation (b) Correct Orientation

The rate of reaction depends on the rate of successful collisions between reactant particles. Reacting particles must collide with sufficient energy to form the **activated complex** (a temporary species formed by the reactant particles as a result of the collision before they form the product). The more successful collisions there are, the more the activated complex leads to the rate of a reaction being faster.

In the molecular view of the matter, it is postulated that chemical reactions depend on the collisions between the reacting particles – atoms, molecules or ions. Hence, the collision theory can be stated as below.

Reacting particles (atoms, molecules, or ions) must collide in the correct orientation with sufficient energy to overcome the energy barrier to react.

According to the collision theory, a reaction will speed up if (i) the frequency of collision increases and (ii) the proportion of particles with energy that is greater than the activation energy increases.

Collision theory can be used to explain the main factors such as concentration, temperature, pressure, and particle size, affecting the rate of chemical reactions.

(b) Activation Energy

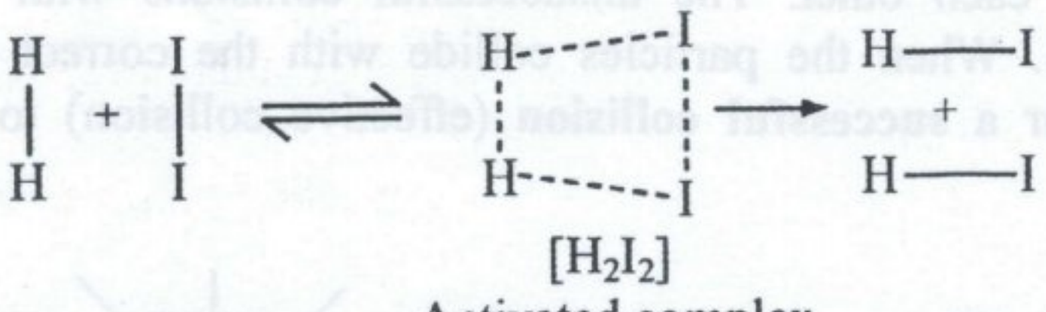
In terms of the collision theory, for a chemical reaction to occur, the colliding molecules must possess at least a certain minimum energy necessary to rearrange the original bonds breaking or new bonds forming. **The activation energy (E_a)** is the minimum energy that reactant particles must possess for a successful collision to take place in a reaction. During the progress of a reaction, an unstable intermediate which is known as an activated complex, having required minimum energy, is formed before producing a product.

For example, a hydrogen molecule and an iodine molecule collide to form an unstable intermediate $[H_2I_2]$ which exists for a short time and then breaks up to form two molecules of hydrogen iodide.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons [H_2I_2] \longrightarrow 2HI\,(g)$$

Activated complex

It can be shown diagrammatically as follows:



$[H_2I_2]$
Activated complex

In order to get the product HI, the reactants must pass through a short-lived, high-energy **transition state**. The minimum energy that needs to be reached in this state is equal to the activation energy (E_a) for that reaction. Hence, the activation energy represents an energy barrier for the reaction, and it has a different value in different reactions.

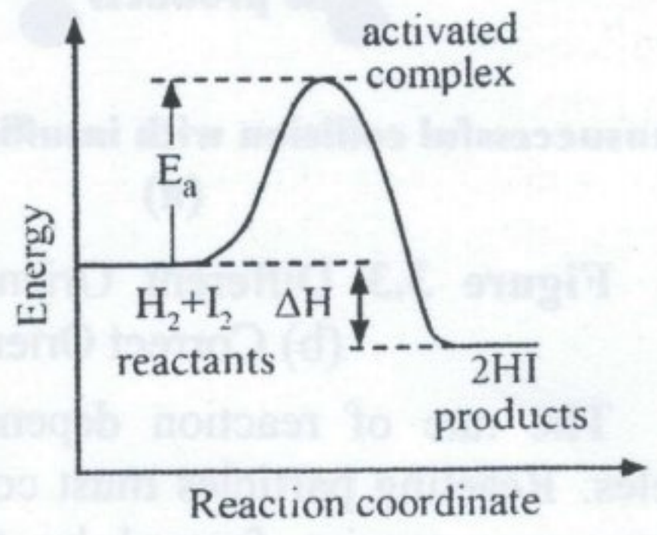


Figure 3.4 Energy Profile Diagram for the Exothermic Reaction between Hydrogen and Iodine

Figure 3.4 shows the diagram of energy change when H_2 gas reacts with I_2 gas to form HI as a product. In this reaction, since the final product HI has less energy than that of the reactants, the reaction is the exothermic reaction. Some energy is released when the activated complex $[H_2I_2]$ leads to the formation of the products. When there is sufficient energy to overcome the energy barrier, the formation of the product is favourable. If the energy is not enough, it cannot overcome the energy barrier and the decomposition of the product, that is, back to reactants will occur.

A high E_a means that relatively few collisions have the required energy to produce the activated complex, and hence, the reaction rate is slow. With a low E_a, more collisions have sufficient energy to react, and the reaction rate is fast.

REVIEW QUESTIONS

(1) (a) Name the theory that is used to explain the rate of a reaction.
(b) What are the main factors for a chemical reaction to speed up?

(2) (a) What type of orientation will be important to produce a product? Explain why.
(b) Name the state which the reactants must pass through to get the products.

(3) (a) What does the activation energy mean?
(b) Three reactions, A, B, and C have activation energies of 8, 10 and 15 kcal mol^{-1}, respectively. Which of these reactions will occur most rapidly at 25 °C? Explain your answer.

Key Terms

- **Collision theory** states that a chemical reaction only takes place when two reacting molecules collide in the correct orientation with sufficient kinetic energy.
- **Successful collision** is a collision that causes a chemical reaction.
- **Activated complex** is a temporary unstable arrangement of atoms that may form products or break apart to reform the reactants.
- **Activation energy** is the minimum amount of energy that reacting particles must have to form the activated complex and lead to a reaction.
- **Transition state** (also known as an intermediate state) is a highly energetic state that would be highly unstable.

3.3 FACTORS AFFECTING REACTION RATES

Although a reaction needs to take place rapidly, it need not be dangerous. For example, the controlled burning of fuel in an internal combustion engine is required to avoid fire or explosion. On the other hand, some undesirable reactions, such as the spoiling of food, need to take place more slowly. Thus, to bring the reaction under control in desirable ways, what factors determine its rate will be studied in this section.

(a) Effect of Concentration of Reactants

For many reactions involving liquids or gases, increasing the concentrations of the reactants increases the rate of reactions. The effect of concentration on the rate of reaction can be explained by the collision theory. If more molecules or ions of the reactants are in the reaction area, then there is a greater chance of more effective collisions per unit time and, thus, more reactions will occur. For example, zinc granule reacts fairly slowly with 1.0 mol dm^{-3} dilute hydrochloric acid but much faster with the more concentrated 6.0 mol dm^{-3} hydrochloric acid as a function of time (Figure 3.5). The higher the concentration of reactant hydrochloric acid, more collisions on the surface of the zinc will occur throughout the time period (Time 1 to Time 3). Hence, the reactant zinc will be used up more quickly and the rate of reaction will be faster.

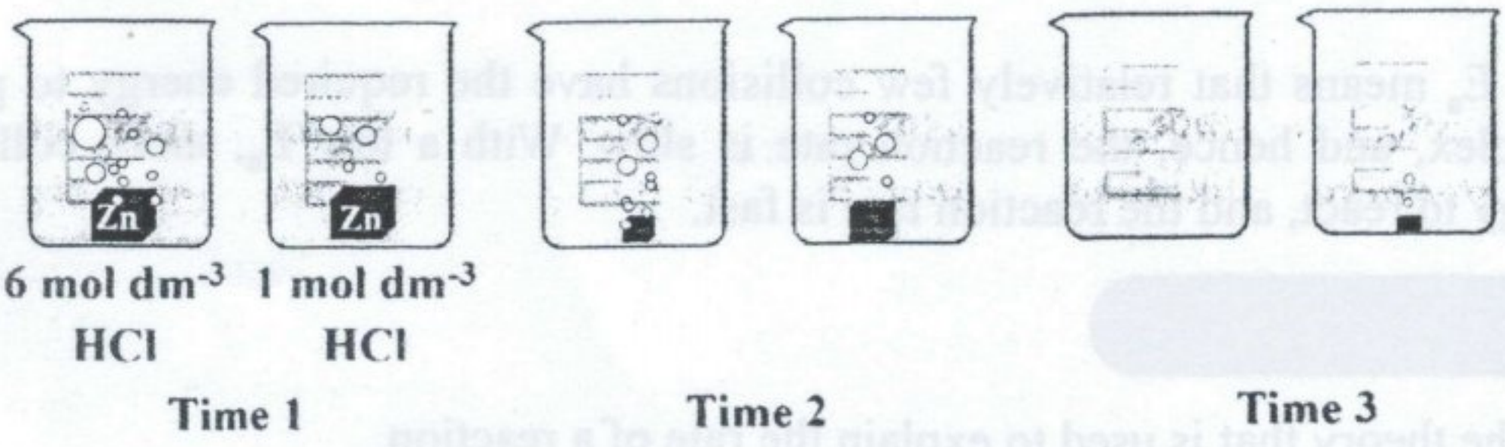


Figure 3.5 The Progress of Reactions of Zn with Different Concentrations of HCl during Three Periods of Time

$$Zn\ (s) + 2HCl\ (aq) \longrightarrow ZnCl_2\ (aq) + H_2\ (g)$$

(b) Effect of Particle Size

In reactions involving solids, a reaction occurs at the boundary surface between reactants. The rate of a reaction involving a solid reactant is increased by increasing the surface area of the solid. The smaller the particle size, the larger the surface area will be. If the surface is larger, it will be hit by more moving reacting particles per unit time, and the rate of reaction will be faster.

For example, aluminium foil reacts moderately with sodium hydroxide solution only when warmed, but powdered aluminium of the same mass reacts rapidly in the cold. Reducing the size of particles increases the surface area, increases the number of collisions per second, increases the number of effective collisions, and thus increases the rate of reaction. Large pieces of wood are difficult to ignite whereas small pieces burn more rapidly.

(c) Effect of Pressure

Changing the pressure does not affect the rate of reaction that only involves solids or liquids. But pressure affects the rate of a reaction involving gases. Increasing the pressure increases the speed of the reaction. The pressure is inversely proportional to the volume of a gas at a constant temperature (Figure 3.6). At low pressure, the volume becomes larger, the number of collisions of gaseous molecules is smaller, and thus, the rate of reaction is slower. At high pressure, the volume becomes smaller, the number of collisions is greater, and thus, the rate of reaction is faster.

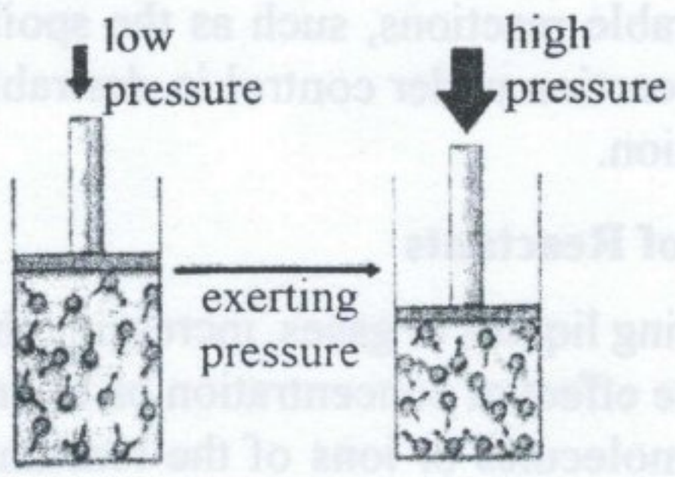
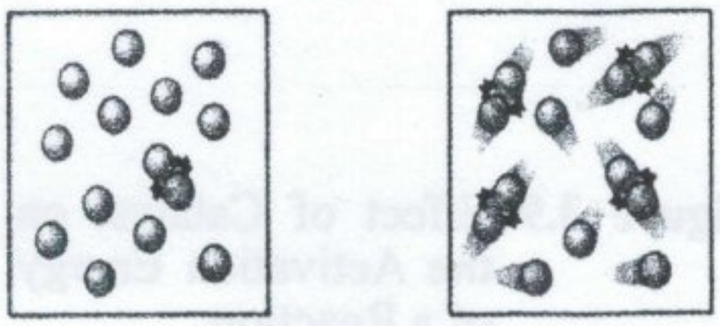


Figure 3.6 Effect of Pressure on the Collision of Gaseous Molecules

For example, food can cook faster in a pressure cooker than in a pot, because trapped steam becomes hotter as the pressure increases. causing more water molecules to collide and the reaction to speed up.

(d) Effect of Temperature

Most chemical reactions react faster at a high temperature than at a low temperature. The kinetic energy of a gas is directly proportional to the temperature. Therefore, increasing the temperature also increases the kinetic energy, which means that the molecules move faster and collide more frequently with sufficient activation energy for the reaction to proceed (Figure 3.7). Thus, the number of effective collisions per second of the reacting particles increases, and hence, the rate of reaction increases. For instance, the time required to hard-boil an egg in water is much shorter at 100 °C than at 80 °C. On the other hand, foods are cooled or frozen to slow down the chemical reactions that result in the spoiling of food, the ripening of fruit and the souring of milk.



Less collision at low temperature **More collision at high temperature**

Figure 3.7 Effect of Temperature on Collision of Particles with Energy

The effect of temperature on reaction rates can also be explained by using the energy distribution curve also known as the Boltzmann distribution. In general, the area under the curve represents the number of particles within a certain energy range. The shaded area shows the number of particles with energy greater than the activation energy. Let us suppose that chemical reactions take place only if the collided particles possess activation energy, E_a.

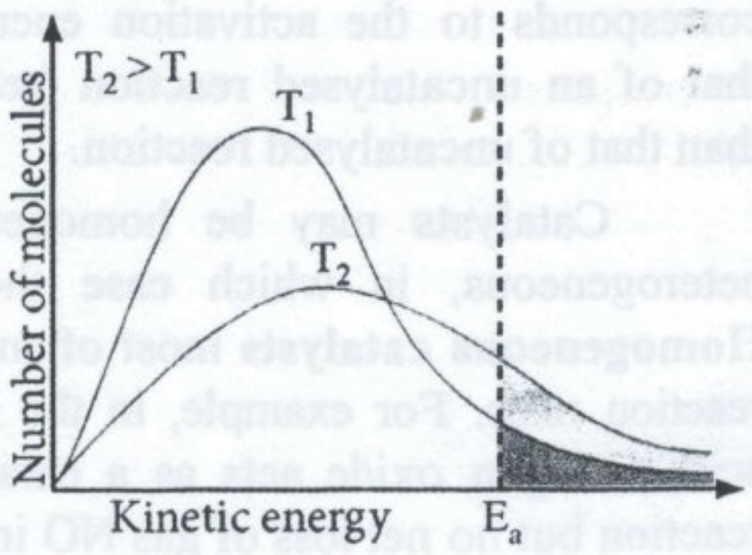


Figure 3.8 Boltzmann Distribution of Molecular Energies at Temperatures T_1 and T_2, Showing the Activation Energy

Figure 3.8 is the plot of energy distribution curves at two different temperatures. The area under the distribution curve at temperature T_1 gives the fraction of the number of molecules having particular energy while the shaded area represents the number of molecules with energy greater than the activation energy, E_a. When the temperature is increased to T_2, the shape of the distribution curve changes. It flattens and spreads out as shown in the figure, showing that the fraction of molecules with energy greater than E_a is much larger at the higher temperature, T_2. The fraction of molecules with energy greater than the activation energy will move faster and collide more often by increasing the temperature. Hence, the reaction becomes faster. That is, increasing the temperature can lead to increasing the rate of a reaction. Generally, for a ten degrees rise in temperature, this area under the curve approximately doubles as does the rate of reactions.

(e) Effect of Catalysts

A catalyst is defined as a substance which alters the rate of a chemical reaction but remains chemically unchanged at the end of the reaction. Most catalysts make chemical reactions go faster. These catalysts are known as **positive catalysts**. The most common positive catalysts used in the chemical industries are iron in the Haber Process for manufacturing ammonia; vanadium(V) oxide or platinised asbestos in the Contact Process for manufacturing sulphur trioxide; and manganese(IV) oxide in the preparation of oxygen from hydrogen peroxide.

Sometimes, a chemical reaction needs to go more slowly or suppress unwanted reactions. For instance, the alcohol acts as a catalyst to slow down the oxidation of sodium sulphite to sodium sulphate. This kind of catalyst is known as a **negative catalyst**.

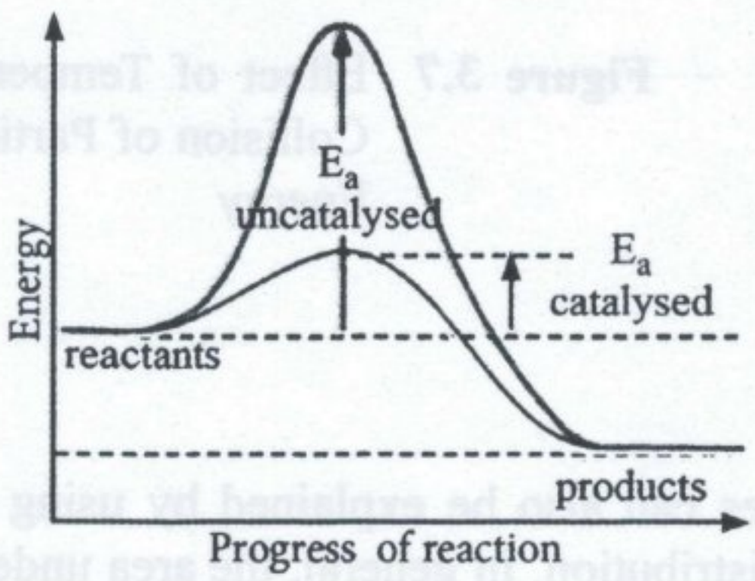


Figure 3.9 Effect of Catalyst on the Activation Energy of a Reaction

Generally, the catalysts provide an alternative pathway for the reaction with lower activation energy, and thus increasing the reaction rate. Figure 3.9 is the energy diagram which shows the reaction progress of uncatalysed and catalysed reactions. In the diagram, the pathway corresponds to the activation energy of a catalysed reaction (blue curve) being less than that of an uncatalysed reaction (red curve), and thus the rate of catalysed reaction is faster than that of uncatalysed reaction.

Catalysts may be homogeneous, that is, uniformly mixed with the reactants, or heterogeneous, in which case the catalyst and the reactants ar in different **phases**. **Homogeneous catalysts** most often catalyse the gaseous and aqueous reactions to increase their reaction rates. For example, in the manufacturing process (Lead chamber process) of sulphuric acid, nitrogen oxide acts as a catalyst in the oxidation of sulphur dioxide to speed up the reaction but no net loss of gas NO in the overall reaction.

$$2SO_2\,(g) + O_2\,(g) \xrightarrow{NO} 2SO_3\,(g)$$

Most **heterogeneous catalysts** are solids that catalyse either gaseous or liquid reactants. The reactions take place on the surface of the solid catalyst to speed up. For example, in ammonia oxidation process (Ostwald process), Pt - Rh catalyst speeds up the reaction.

$$4NH_3\,(g) + 5O_2\,(g) \xrightarrow[800\ ^\circ C]{Pt\text{ - }Rh} 4NO\,(g) + 6H_2O\,(g)$$

Catalysts are important for the proper functioning of the biological systems. **Enzymes** act as biocatalysts for specific biochemical reactions in living systems. The most well-known digestive enzymes, ptyalin in saliva and pepsin in gastric juice, catalyse to hasten the breakdown of large molecules, such as starch and protein, into simpler molecules. In general, the reaction rate using enzymes is much faster than inorganic catalysts, often increased by a factor of 10^6 to 10^{12}.

(f) Effect of Light

Some chemical reactions obtain the energy they need from light. Reactions that are initiated by light are called **photochemical reactions**. The brighter the light, the faster is the reaction. If the intensity of light (visible or ultraviolet) is greater, the more reactant molecules gain the required energy (activation energy) and the faster the reaction speed. When the reactant molecules absorb the light (hν), a photochemical reaction takes place, such as photosynthesis in green plants, a chain reaction in ozone depletion, and the decomposition of silver bromide in photographic films. The reaction between hydrogen and chlorine is extremely slow in the dark, but it becomes explosive when the reaction mixture is exposed to intense sunlight via a chain reaction.

$$H_2\,(g) + Cl_2\,(g) \longrightarrow 2HCl\,(g) \quad \text{slow}$$
$$H_2\,(g) + Cl_2\,(g) \xrightarrow{h\nu} 2HCl\,(g) \quad \text{fast}$$

REVIEW QUESTIONS

(1) (a) List any five factors that affect the rate of reactions.
(b) Substances burn more rapidly in pure oxygen than in air. Explain why.

(2) Give a reason for each of the following statements:
(a) The large crystals of sugar burn slower than finely ground sugar.
(b) The powdered calcium carbonate reacts with 0.5 mol dm^{-3} hydrochloric acid for 2 min while it takes 40 s with 1.0 mol dm^{-3} hydrochloric acid.
(c) Hydrogen and chlorine react extremely slowly in the dark, but the reaction becomes explosive in the bright sunlight.
(d) Foods readily spoil at room temperature at a faster rate than when foods are refrigerated.

(3) What is the difference between a homogeneous catalyst and a heterogeneous catalyst? Give two examples for each.

Key Terms

- **Catalyst** is a substance that alters the rate of a chemical reaction but remains chemically unchanged at the end of the reaction.
- **Positive catalyst** is a catalyst that increases the rate of a chemical reaction.
- **Negative catalyst** is a catalyst that decreases the rate of a chemical reaction.
- **Phase** is a portion of a physical state (solid, liquid, gas) that is homogeneous throughout, and can be separated physically from other phases.
- **Homogeneous catalyst** is a catalyst which is in the same phase as the reactants in a catalysed reaction.
- **Heterogeneous catalyst** is a catalyst which is in a different phase from the reactants in a catalysed reaction.
- **Enzymes** are proteins that act as catalysts for specific biochemical reactions.
- **Photochemical reaction** is a chemical reaction initiated by the absorption of energy in the form of light, resulting in specific products.

Chemistry in Society

- When large amounts of flammable powdered substances collect in grain elevators, coal mines, and chemical industries, violent explosions can occur.
- Storage of preserved foods at a sub-zero temperature in a refrigerator is effective for slowing the rate of bacterial decay and also helping keep food fresh for longer periods of time.
- At high altitudes with low temperature less than 100 °C, it takes a long time (about 30 min) to boil an egg. In the plains with high pressure, water boils at 100 °C, so the boiling time is shorter than that on the hills.
- In many industrial processes, enzymes from organisms (usually bacteria) are widely used in specific reactions such as the conversion of glucose to sweeter-tasting fructose, the manufacture of new antibiotics and the manufacture of laundry detergents.
- Corrosion inhibitors like imidazoline and quaternary amine prevent H_2S and CO_2 corrosion. Volatile corrosion inhibitors (VCI) such as morpholine or hydrazine prevent corrosion in boilers. Wrapping metals in volatile corrosion inhibitor-coated paper is common short-term protection against moisture and humidity.

EXERCISES

Q 1 to Q 4 (Remembering and Understanding)

1. For each of the following, say whether the statement is TRUE or FALSE. If the statement is FALSE, correct it.
   (a) The unit of a reaction rate depends only on the physical states of reactants.
   (b) A rate is always expressed as a positive quantity.
   (c) If the concentration of a substance increases, the kinetic energy of the particles also increases.
   (d) The rates of chemical reactions are increased by the catalysts raising the activation energy of the reactions.
   (e) The volumes of gases are greatly affected by pressure.
2. Fill in the blanks with a suitable word or phrase or numerical value with units as necessary.
   (a) The unit for the rate of a chemical reaction in solution is _____.
   (b) The _____ energy required to form the activated complex is called the activation energy.
   (c) A catalyst which is in the different phases of the reactants is known as _____ catalyst.
   (d) The correct _____ of reactant molecules leads to the formation of products.
   (e) More molecules have sufficient energy to react, so the _____ of reaction is increased.
3. Select the correct units, phrases, word or words given in the brackets.
   (a) The reaction time is (inversely proportional, directly proportional, equal) to the rate.
   (b) The experimental unit for the rate of formation of hydrogen gas collected in the syringe is ($g\ min^{-1}$, $mol\ dm^{-3}\ min^{-1}$, $cm^3\ min^{-1}$).

(c) The reaction rate of marble chips ($CaCO_3$) with 1 mol dm^{-3} HCl aqueous solution is slow. If 3 mol dm^{-3} HCl aqueous solution is used instead of 1 mol dm^{-3} HCl, the rate of reaction will (decrease, increase, constant).

(d) In a chemical reaction, the rate may be expressed using the units of (mol^{-1} s^{-1}, mol dm^3 s^{-1}, mol dm^{-3} s^{-1})

(e) (Collision with enough energy, Every collision, Collision with low energy) leads to the chemical reaction to proceed.

4. Match each of the items given in List A with the appropriate item in List B.

List A	List B
(a) enzymes	(i) sufficient energy
(b) smaller particles	(ii) reaction by light
(c) negative catalyst	(iii) biocatalysts
(d) photochemical reaction	(iv) larger surface area
(e) effective collision	(v) slow down the rate of reaction

Q 5 to Q 13 (Analysing and Problem Solving)

5. A number of different reactions take place. The table below shows the number of moles of a reactant that are used up at a particular time for each reaction.

Reaction	Mole used up	Time	Reaction rate
1	2	30 s	
2	5	2 min	
3	1	1.5 min	
4	3.2	1.5 min	
5	5.9	30 s	

(i) Complete the table by calculating the rate of each reaction.
(ii) Which is the fastest reaction?
(iii) Which is the slowest reaction?

6. Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:

(a) $CaCO_3$ (s) + 2HCl (aq) $\longrightarrow$ $CaCl_2$ (aq) + H_2O (l) + CO_2 (g)
(b) $4NH_3$ (g) + $5O_2$ (g) $\longrightarrow$ 4NO (g) + $6H_2O$ (g)
(c) CH_4 (g) + Br_2 (g) $\longrightarrow$ CH_3Br (g) + HBr (g)

7. The following two reactions occur simultaneously in separate reaction vessels.

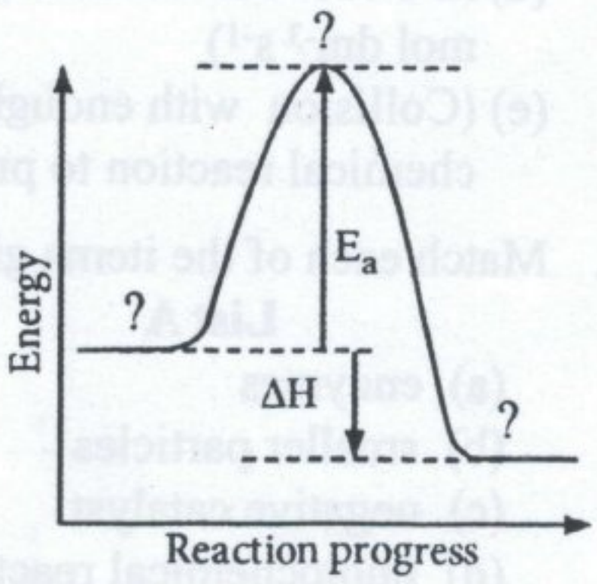
Mg (s) + Cl_2 (g) $\longrightarrow$ $MgCl_2$ (s) ; 2Na (s) + Cl_2 (g) $\longrightarrow$ 2NaCl (s)

After 1 min, 2 g of $MgCl_2$ has been produced in the first reaction.

(i) How many moles of $MgCl_2$ are produced after one minute?
(ii) Calculate the rate of the reaction using the amount of product that is produced.
(iii) Assume that the second reaction also proceeds at the same rate. Calculate the number of moles of NaCl produced after 1 min and the mass (in g) of sodium that is needed for this reaction to take place. (Mg = 24, Na = 23, Cl = 35.5)

8. (a) The glowing splint will burn more vigorously in pure oxygen than oxygen in the air. Explain why.
   (b) Would it produce the same results if burning sawdust is used instead of glowing splint? Explain your answer.

9. Use the energy diagram for the reaction of carbon monoxide and nitrogen dioxide to form carbon dioxide and nitrogen oxide to answer the following questions.



   (i) Complete the energy diagram.
   (ii) What kind of reaction is represented by this diagram, endothermic or exothermic? Give reasons.
   (iii) What does the symbol E_a represent?
   (iv) What does the symbol ΔH represent?

10. Two gases X and Y have been filled in a container. What effect will the following changes have on the rate of the reaction between these gases? X+Y ⟶ Products
   (i) The pressure is doubled.
   (ii) The number of molecules of gas X is doubled.
   (iii) The temperature is decreased at a constant volume.

11. In the Ostwald process for manufacturing nitric acid, ammonia oxidation occurs slowly as the following reaction.

$$NH_3\,(g) + O_2\,(g) \xrightarrow[800\ °C]{\text{Pt-Rh}} NO\,(g) + H_2O\,(g)$$

   (i) Write down the balanced chemical equation for the reaction.
   (ii) Which factors affect the speed of this reaction?
   (iii) What type of catalyst is Pt-Rh in this reaction?

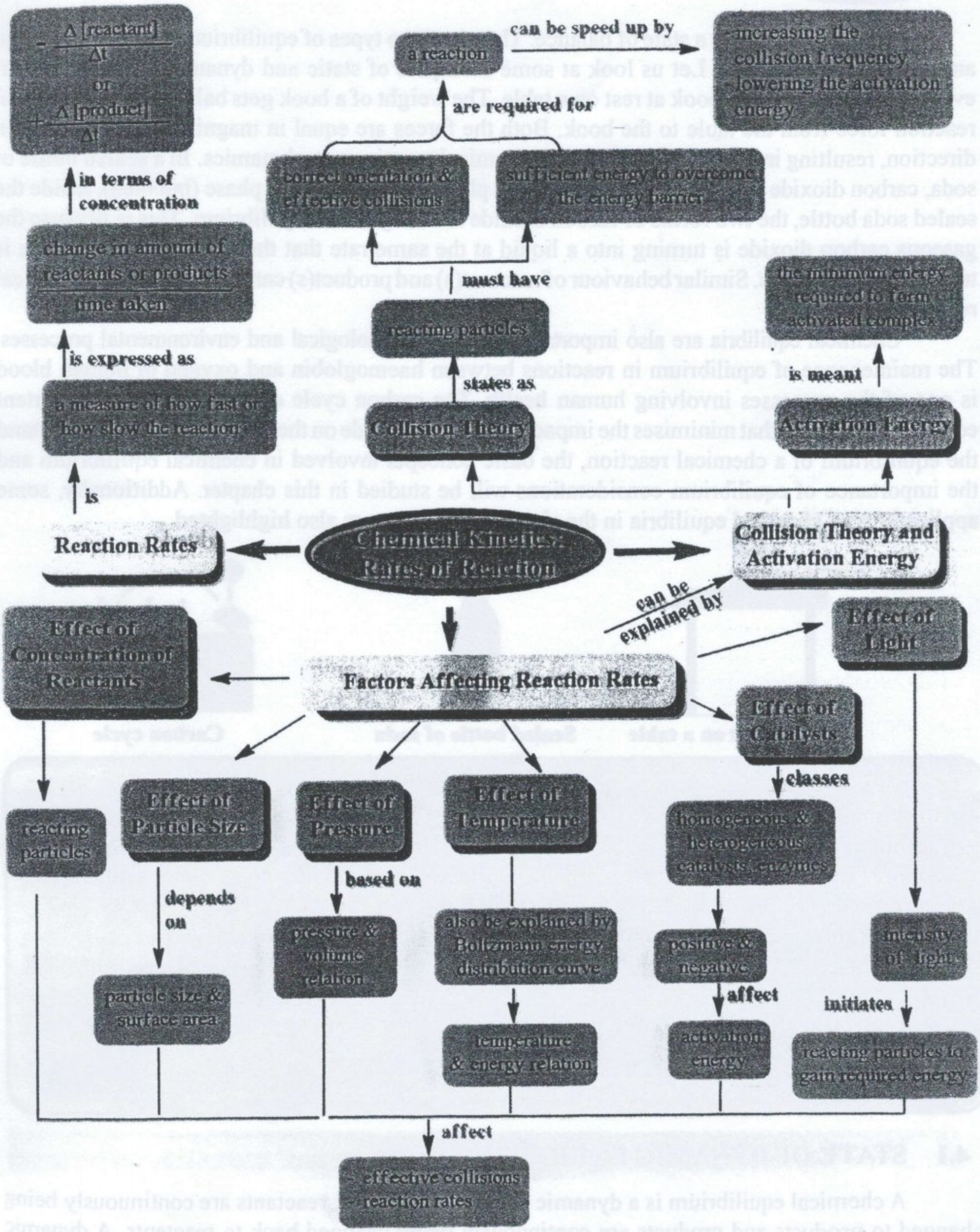
12. A sample of 5 g of calcium carbonate powder reacts with 20 cm^3 of a 0.1 mol dm^{-3} solution of hydrochloric acid. The gas that is produced at a temperature of 25 °C is collected in a gas syringe.
   (a) Write the rate expression in terms of the reactant (calcium carbonate) and the gaseous product.
   (b) The rate of the reaction is determined by measuring the volume of gas that is produced in the first minute of the reaction. What would happen to the rate of the reaction if -
      (i) a lump of calcium carbonate of the same mass is used?
      (ii) 40 cm^3 of 0.1 mol dm^{-3} hydrochloric acid is used?

13. (a) How would you classify whether the following catalysed reaction is heterogeneous or homogeneous catalysis?

$$2SO_2\,(g) + O_2\,(g) \xrightarrow{V_2O_5} 2SO_3\,(g)$$

   (b) Explain how a catalyst affects the rate of reaction in terms of activation energy.

CHAPTER REVIEW
(Concept Map)

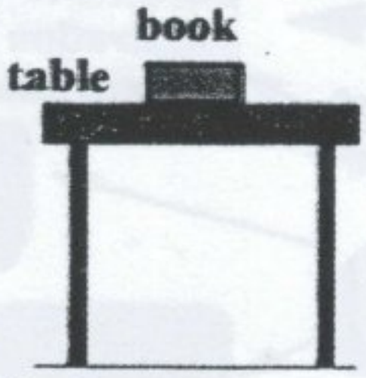


CHAPTER 4

CHEMICAL EQUILIBRIUM

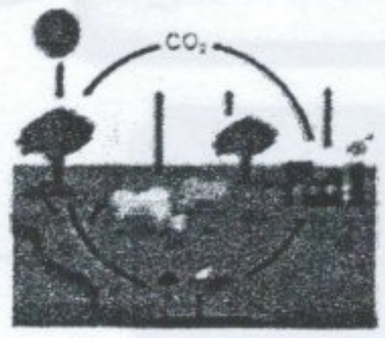
Equilibrium means a state of balance. There are two types of equilibrium; static equilibrium and dynamic equilibrium. Let us look at some examples of static and dynamic equilibria in our everyday life. Consider a book at rest on a table. The weight of a book gets balanced by the normal reaction force from the table to the book. Both the forces are equal in magnitude but opposite in direction, resulting in static equilibrium. All chemical reactions are dynamics. In a sealed bottle of soda, carbon dioxide is present in both the liquid phase and the gaseous phase (bubbles). Inside the sealed soda bottle, the two forms of carbon dioxide are in dynamic equilibrium. This is because the gaseous carbon dioxide is turning into a liquid at the same rate that the liquid carbon dioxide is turning back into a gas. Similar behaviour of reactant(s) and product(s) can be observed in a chemical reaction.

Chemical equilibria are also important in numerous biological and environmental processes. The maintenance of equilibrium in reactions between haemoglobin and oxygen in human blood is one of the processes involving human health. The carbon cycle contributes to the important equilibrium process that minimises the impacts of carbon dioxide on the environment. To understand the equilibrium of a chemical reaction, the basic concepts involved in chemical equilibrium and the importance of equilibrium considerations will be studied in this chapter. Additionally, some applications of chemical equilibria in the chemical industry are also highlighted.



Book at rest on a table

Sealed bottle of soda



Carbon cycle

Learning Outcomes

After completing this chapter, students will be able to:

- explain the reversible reaction and the dynamic nature of a chemical equilibrium;
- apply Le Chatelier's Principle to explain the effects of changes in concentration, temperature, or pressure, on a closed system at equilibrium;
- predict the direction of an equilibrium shift by any change in conditions;
- write an expression for the equilibrium constants K_c, and K_p from a given balanced chemical equation;
- calculate the values of equilibrium constants and concentration of each substance from the appropriate data;
- explain how equilibrium principles are applied to the production of industrial chemicals.

4.1 STATE OF DYNAMIC EQUILIBRIUM

A chemical equilibrium is a dynamic equilibrium; that is, reactants are continuously being changed to products and products are continuously being changed back to reactants. A dynamic equilibrium exists once a reversible reaction occurs.

(a) Reversible Reaction and Equilibrium

Many chemical reactions go to completion. For example, fuels are burned in the air to produce carbon dioxide and water, and the reaction stops when all the fuels have been used up. The products cannot be converted back to reactants. But, some reactions do not go to completion, and they can be reversed. There is the **forward reaction** where reactants are converted into products, and the **reverse reaction** where the products are converted back into the starting reactants under the appropriate conditions. These reactions are **reversible reactions**.

The following is an example of reversible reaction which can be used as a qualitative illustration of chemical equilibrium.

$$A + B \underset{\text{reverse reaction}}{\overset{\text{forward reaction}}{\rightleftharpoons}} C$$

The symbol $\rightleftharpoons$ is used to represent the reversible reaction. In the forward reaction, reactants A and B combine to form product C. In the reverse reaction, C decomposes into A and B. So, a reversible reaction is one that can occur in both the forward and reverse directions, and the conversion of reactants to products and the conversion of products to reactants occur simultaneously. Reversible reactions that happen in a closed system eventually reach equilibrium. When the rates of the forward and reverse reactions balance, the reversible reaction is in equilibrium.

(b) Dynamic Nature of Equilibrium

If a reversible reaction is in a **closed system,** the system can reach a state called a **dynamic equilibrium**. In dynamic equilibrium, the forward and reverse reactions do not stop; rather, they continue to occur at the same rate, leading to constant concentrations of the reactants and products. Figures 4.1 (a) and (b) depict the concentration changes of the reactant and product and the reaction rates with respect to time.

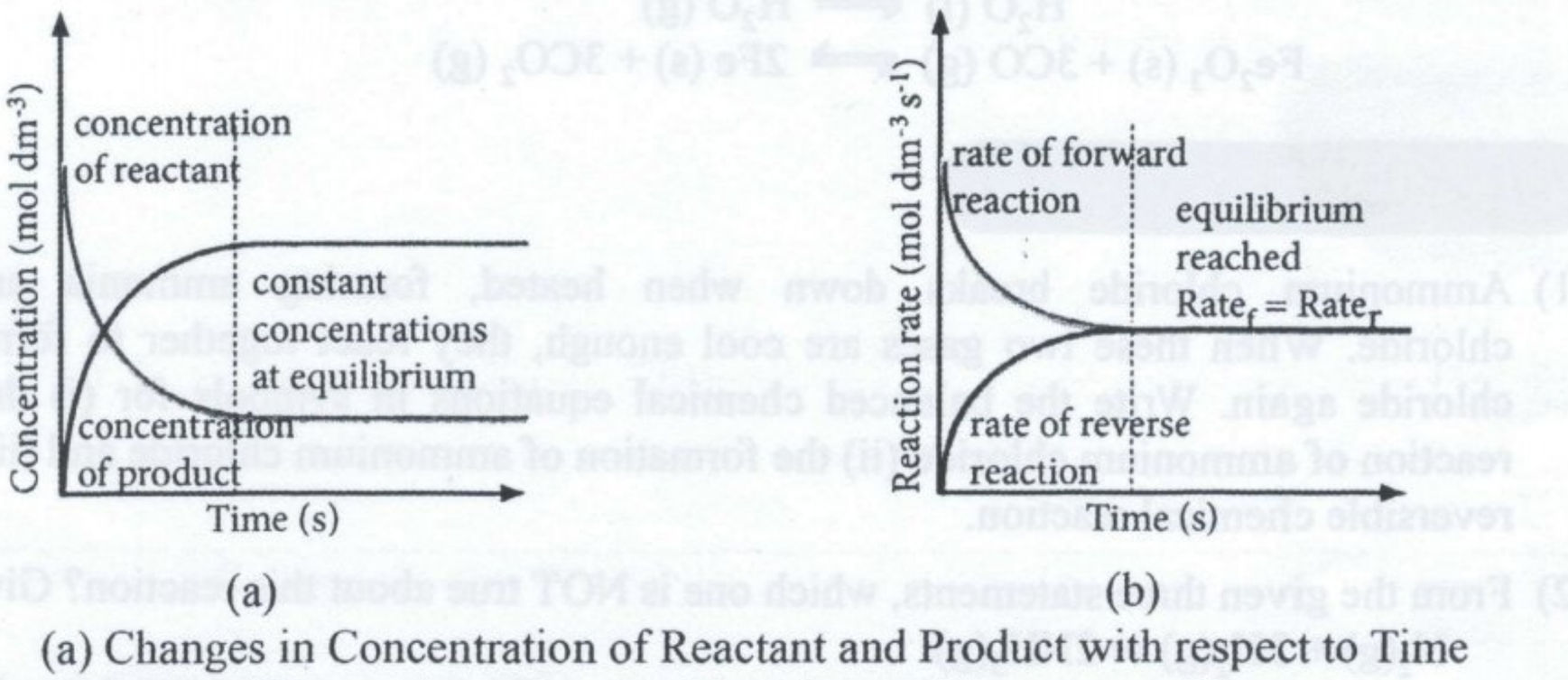


Figure 4.1 (a) Changes in Concentration of Reactant and Product with respect to Time
(b) Rates of Forward and Reverse Reactions with respect to Time

As shown in Figure 4.1 (a), it can be seen that, generally, the reaction begins with only the concentrations of reactants and there are no products formed. As the reaction proceeds towards equilibrium, the concentrations of reactants gradually decrease, whereas the concentrations of products gradually increase. After a system has reached equilibrium, as shown by the dotted line, the concentrations of all substances remain constant.

As depicted in Figure 4.1 (b), the rate of the forward reaction is high and the rate of the reverse reaction is low initially. As the reaction proceeds, the rate of the forward reaction decreases and the rate of the reverse reaction increases until both reactions occur at the same rate. As indicated by the dotted line, the equilibrium is reached when the two rates are equal. In equilibrium, the forward and reverse reactions are still proceeding at an equal rate. Thus, the equilibrium is dynamic in nature. This state of chemical equilibrium is known as dynamic equilibrium. The above reaction in dynamic equilibrium may be represented by the reversible equation as below.

$$\text{Reactants} \underset{\text{reverse reaction}}{\overset{\text{forward reaction}}{\rightleftharpoons}} \text{Products}$$

Generally, in chemical equilibrium, the reaction is still proceeding at equal rates for the forward and reverse reactions, and the concentrations of the reactants and products remain constant.

(c) Homogeneous and Heterogeneous Chemical Equilibria

Based on the phase of the reactants and products, chemical equilibrium can be classified into homogeneous and heterogeneous chemical equilibria.

(i) Homogeneous chemical equilibrium

In homogenous chemical equilibrium, the reactants and the products of chemical equilibrium are all in a single phase. For example,

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$$

(ii) Heterogeneous chemical equilibrium

In heterogeneous chemical equilibrium, the reactants and the products of chemical equilibrium are present in more than one phase. Any combination of solid, liquid, or gas states, as well as solutions, can exist. For example,

$$H_2O\,(l) \rightleftharpoons H_2O\,(g)$$
$$Fe_2O_3\,(s) + 3CO\,(g) \rightleftharpoons 2Fe\,(s) + 3CO_2\,(g)$$

REVIEW QUESTIONS

(1) Ammonium chloride breaks down when heated, forming ammonia and hydrogen chloride. When these two gases are cool enough, they react together to form ammonium chloride again. Write the balanced chemical equations in symbols for (i) the breakdown reaction of ammonium chloride (ii) the formation of ammonium chloride and (iii) the overall reversible chemical reaction.

(2) From the given three statements, which one is NOT true about this reaction? Give a reason.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(i) It is at equilibrium. (ii) It is a heterogeneous equilibrium reaction. (iii) It is a homogeneous equilibrium reaction.

(3) Which of the following equilibria are homogeneous and which are heterogeneous?

(i) $2NaHCO_3\,(s) \rightleftharpoons Na_2CO_3\,(s) + H_2O\,(g) + CO_2\,(g)$ (ii) $C\,(s) + 2H_2\,(g) \rightleftharpoons CH_4\,(g)$

(iii) $C_2H_4\,(g) + H_2\,(g) \rightleftharpoons C_2H_6\,(g)$ (iv) $2Hg\,(l) + O_2\,(g) \rightleftharpoons 2HgO\,(s)$

Key Terms

- **Reversible reaction** is a reaction that can proceed in the forward as well as in the reverse directions under the appropriate conditions.
- **Closed system** is a system that allows energy to enter and exit, but matter can neither be gained nor lost.
- **Dynamic equilibrium** is a chemical equilibrium in which the reaction is still proceeding at equal rates of the forward and reverse reactions, and the concentrations of the reactants and products remain constant.
- **Homogeneous equilibrium** is one in which the reactants and the products of chemical equilibrium are all in a single phase.
- **Heterogeneous equilibrium** is one in which the reactants and the products of chemical equilibrium are all in more than one phase.

4.2 Le CHATELIER'S PRINCIPLE AND FACTORS AFFECTING THE CHEMICAL EQUILIBRIUM

As mentioned in Section 4.1(b), at dynamic equilibrium, the rates of forward and reverse reactions are equal, and thus the concentrations of reactants and products remain constant. In the previous chapter, Rates of Reaction, the factors affecting the rate of reaction are described. In this section, what effect these factors may have on the position of equilibrium of a reaction will be considered.

(a) Le Chatelier's Principle

Le Chatelier's principle is a qualitative guide to the effect of changes in concentration, temperature, and pressure on a system at equilibrium. When one of these factors (stress) changes, the position of chemical equilibrium is effectively altered. This idea was discovered by French Chemist Henri Louis Le Chatelier in 1884. Le Chatelier's principle can be stated as below.

If a system is in equilibrium and when any of the factors affecting the chemical equilibrium, such as temperature, pressure, or concentration is changed, the equilibrium shifts (moves) so as to cancel out the effect of the change.

In other words, if one of the factors affecting the system of chemical equilibrium is changed, the system will respond oppositely. This means, that by adding something, the system will react to remove it; by removing something, the system will react to replace it. After that, a new equilibrium will be established.

(b) Factors Affecting the Chemical Equilibrium

Once equilibrium is established in a system, no further change is apparent as long as the external factors remain unchanged. If the external factors are altered, the system will shift to a new state of equilibrium. The changes in concentration, temperature, and pressure of the system (stress) are external factors that affect equilibrium. The greater the stress, the more the direction of the reaction shifts in response to the stress. In some cases, stress causes no shift in the equilibrium, especially when the moles of reactants and products are equal after the change in the pressure of gases. Le Chatelier's principle describes how a chemical equilibrium shifts in response to a stress within an enclosed system.

A change in concentration, temperature, or pressure makes a difference in the amount of product formed in a reaction. However, a catalyst does not affect the equilibrium concentrations and there is no change in equilibrium.

Effect of concentration on equilibrium

A change in the concentration of one of the substances in an equilibrium system affects the equilibrium positions. Adding or removing a reactant or product from a reaction mixture at equilibrium will always disturb the equilibrium. Le Chatelier's principle predicts that in reaction $A + B \rightleftharpoons C + D$, the reaction will shift in the direction that will minimise the change in concentration caused by the addition or removal.

When the concentration of a reactant is increased (by adding more), the system responds by removing the concentration of the reactant. Thus, the reaction proceeds in the forward direction in favour of products. Equilibrium shifts to the right to reestablish equilibrium.

When the concentration of a reactant is decreased (by reducing it), the system responds by adding the concentration of the reactant. Thus, the reaction proceeds in the reverse direction in favour of reactants. Equilibrium shifts to the left to reestablish equilibrium.

When the concentration of a product is increased (by adding more), the system responds by removing the concentration of the product. Thus, the reaction proceeds in the reverse direction in favour of reactants. Equilibrium shifts to the left to reestablish equilibrium.

When the concentration of a product is decreased (by reducing it), the system responds by adding the concentration of the product. Thus, the reaction proceeds in the forward direction in favour of products. Equilibrium shifts to the right to reestablish equilibrium.

Example 1: Predict the effect of an increasing concentration of SCN^- ions on the given equilibrium.

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

pale yellow colourless blood red

Solution: $Fe^{3+}(aq) + SCN^-(aq) \underset{\text{reverse reaction}}{\overset{\text{forward reaction}}{\rightleftharpoons}} FeSCN^{2+}(aq)$

By increasing the concentration of SCN^-, a forward reaction will be favoured. Equilibrium shifts from left to right and more concentration of $FeSCN^{2+}$ will be formed. The colour of the solution becomes a deep red.

Effect of temperature on equilibrium

Changing the temperature can also affect the equilibrium position. The effect of temperature on chemical equilibrium depends upon the heat changes (ΔH) of the reaction and follows Le Chatelier's principle. In other words, the effect of temperature on an equilibrium depends on whether the reaction is exothermic or endothermic. It is important to consider the forward reaction, whether it is exothermic (heat released) or endothermic (heat absorbed). If the forward reaction is exothermic, the reverse reaction will be endothermic. If a thermochemical equation is given, the value of heat change is for the forward reaction. A temperature decrease favours an exothermic reaction, and a temperature increase favours an endothermic reaction.

In the case of exothermic reactions ($A \rightleftharpoons B \quad \Delta H = -$), decreasing the temperature favours the exothermic reaction by releasing heat. Equilibrium shifts towards the forward reaction.

In the case of endothermic reactions ($A \rightleftharpoons B \quad \Delta H = +$), increasing the temperature favours the endothermic reaction by absorbing heat. Equilibrium shifts towards the forward reaction.

Figure 4.2 shows how the equilibrium between N_2O_4 and NO_2 responds to changes in temperature, as an example. The following reaction is the decomposition of N_2O_4 (colourless) to NO_2 (reddish-brown) and it has a positive ΔH. This means that the forward reaction is endothermic and the reverse reaction is exothermic.

$$\underset{\text{colourless}}{N_2O_4\,(g)} \rightleftharpoons \underset{\text{reddish-brown}}{2NO_2\,(g)} \qquad \Delta H = (+)$$

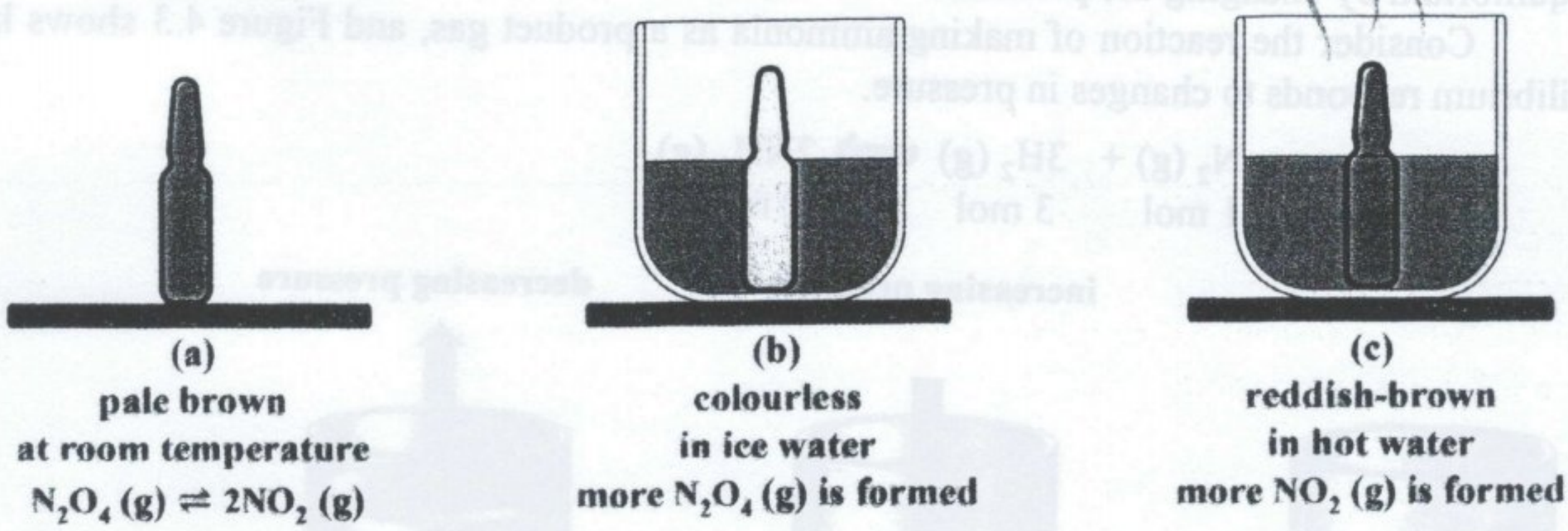


Figure 4.2 Effect of Temperature on the Reaction Equilibrium

In Figure 4.2 (a), the gas mixture of N_2O_4 and NO_2 is in equilibrium at room temperature, and it has a pale brown colour. In Figure 4.2 (b), when the temperature is decreased, it favours the exothermic reaction and the equilibrium shifts to the left. More N_2O_4 is obtained. The colour of the reaction mixture becomes colourless. In Figure 4.2 (c), when the temperature is increased, it favours the endothermic reaction and the equilibrium shifts to the right. More NO_2 is obtained. The colour of the reaction mixture becomes reddish-brown.

Example 2: Using Le Chatelier's principle, what will be the effect of increasing temperature on the given chemical equilibrium? $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) \qquad \Delta H = (-)$

Solution: $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) \qquad \Delta H = (-)$

The forward reaction is an exothermic (heat evolving) reaction and the reverse reaction is an endothermic (heat absorbing) reaction. Increasing the temperature favours the endothermic reaction. The reverse reaction will be favoured. Equilibrium shifts from right to left and more nitrogen and hydrogen gases will be formed.

Effect of pressure on equilibrium

Pressure changes do not markedly affect the solid or liquid phases. However, pressure has a significant effect on the gas phase. The pressure of a gas mixture at a given temperature is determined by the number of gas molecules in a given volume. The effect of pressure depends on the total number of moles of gases on each side of the chemical reactions, that is, reactants and products sides. If the pressure is increased (typically by reducing the volume of the container), then the position of equilibrium will shift towards the side with fewer moles of gas since fewer moles will occupy the smallest volume. This is because the side with fewer moles of gas will have fewer gas molecules to collide with the sides of the container.

In chemical equilibrium, the change of pressure in both liquids and solids can be ignored because their volumes are independent of pressure.

According to Le Chatelier's principle, as pressure increases the equilibrium moves toward the side of the reaction with fewer moles of gas. As pressure decreases, the equilibrium moves toward the side of the reaction with more moles of gas. Moreover, if the number of moles of gas is the same on both sides of the reversible chemical equation, pressure has no effect; there is no shift in equilibrium by changing the pressure.

Consider the reaction of making ammonia as a product gas, and Figure 4.3 shows how equilibrium responds to changes in pressure.

$$\underset{1\text{ mol}}{N_2\,(g)} + \underset{3\text{ mol}}{3H_2\,(g)} \rightleftharpoons \underset{2\text{ mol}}{2NH_3\,(g)}$$

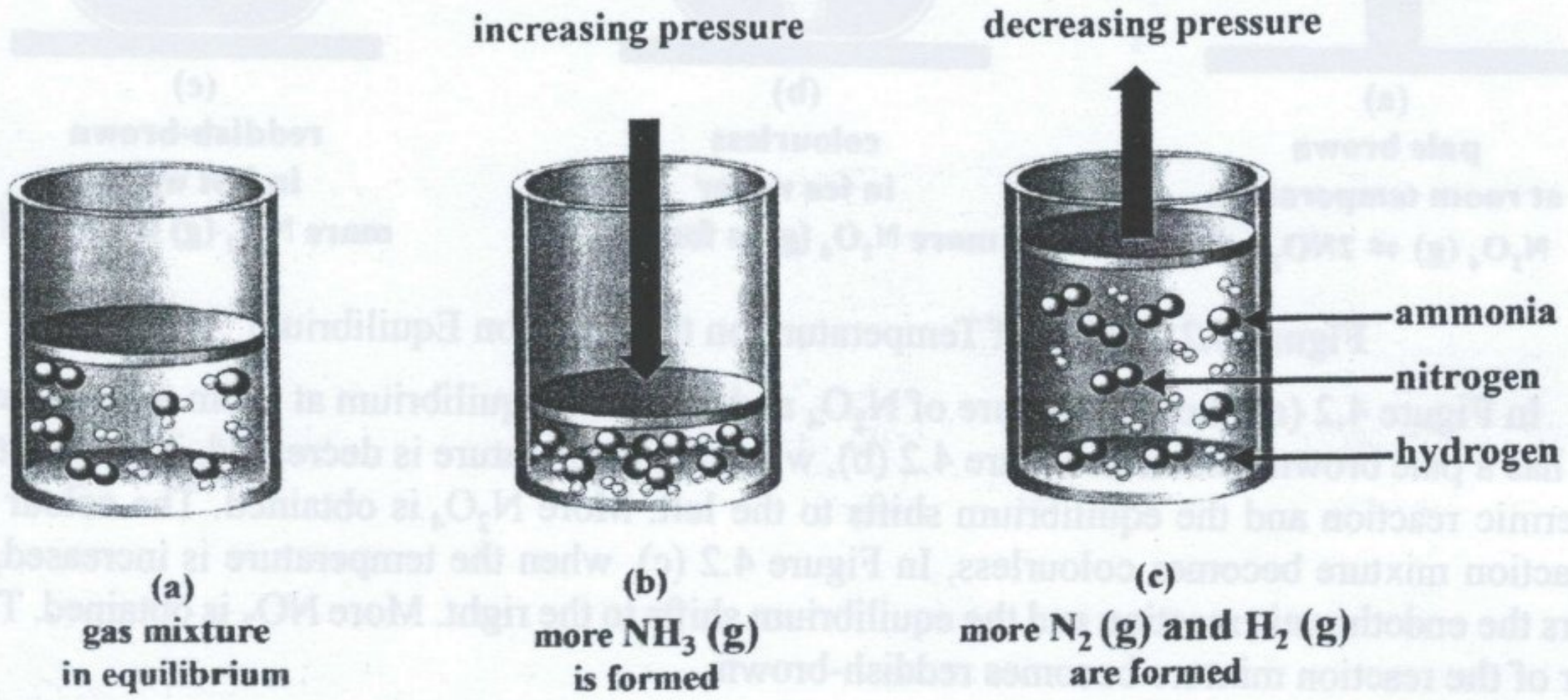


Figure 4.3 Effect of Pressure on the Reaction Equilibrium

In Figure 4.3 (a), the gas mixture of N_2, H_2 and NH_3 are in equilibrium. In Figure 4.3 (b), increasing the pressure by lowering the piston favours fewer moles of the gas. The equilibrium shifts to the right and more ammonia is obtained. In Figure 4.3 (c), decreasing the pressure by raising the piston favours more moles of the gases. The equilibrium shifts to the left and more nitrogen and hydrogen are obtained.

Example 3: Using Le Chatelier's principle, what will be the effect of increasing pressure on the given chemical equilibrium? $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$

Solution:

$$\underset{2\text{ mol}}{2SO_2\,(g)} + \underset{1\text{ mol}}{O_2\,(g)} \rightleftharpoons \underset{2\text{ mol}}{2SO_3\,(g)}$$

In total, there are fewer moles of gas in the forward reaction, and in the reverse reaction are more moles of the gases. According to Le Chatelier's principle, increasing pressure favours fewer moles of gases. The forward reaction will be favoured. Equilibrium shifts from left to right and more sulphur trioxide gas will be formed.

Example 4: Using Le Chatelier's principle, predict the effect of decreasing pressure on the given chemical equilibrium. $4CuO\,(s) \rightleftharpoons 2Cu_2O\,(s) + O_2\,(g)$

Solution:

$$4CuO\ (s) \rightleftharpoons 2Cu_2O\ (s) + O_2\ (g)$$
$$1\ mol$$

Copper(II) oxide and copper(I) oxide are solids and there is no pressure effect on them. So, pressure affects only the oxygen gas. According to Le Chatelier's principle, decreasing the pressure favours more mole of the gas. The forward reaction will be favoured. Equilibrium shifts from left to right and more copper(I) oxide and oxygen gas will be formed.

Example 5: What is the effect of increasing pressure on the given chemical equilibrium?

$$H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$$

Solution:

$$H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$$
$$1\ mol \quad 1\ mol \quad 2\ mol$$

The number of moles of reactants is equal to that of the product. According to Le Chatelier's principle, increasing pressure does not affect the equilibrium.

(c) Applying Le Chatelier's Principle in Industry

Industrial processes are usually designed to give the maximum possible yield of products. The conditions for carrying out the reactions are based on Le Chatelier's principle. The following processes illustrate the application of Le Chatelier's principle in the industry.

(i) Ammonia production

The synthesis of ammonia (Haber process) is a good example of an industrial process that uses Le Chatelier's principle. The chemical equation for the process is shown below.

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g) \qquad \Delta H = (-)$$

Since the reaction is exothermic, the forward reaction is favoured at low temperatures and the reverse reaction at high temperatures. To produce the maximum yield of ammonia, the temperature must be maintained at a level that is low enough to continue the forward reaction. The pressure must be maintained at a high level to get the highest quantity of ammonia. The forward reaction is also favoured by high pressure because there are four moles of reactants for every two moles of product formed. The catalyst used is iron(III) oxide with a small amount of aluminium oxide. The catalyst will speed up the production and this has helped reduce the energy requirements.

(ii) Methanol production

Methanol is an alcohol that is used in fuels, making methyl esters, and creating urea-formaldehyde resin glues through the oxidation of methanol. It is produced from carbon monoxide and hydrogen.

$$CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g) \qquad \Delta H = (-)$$

The forward reaction is exothermic corresponding to the formation of methanol. To produce the maximum yield of methanol, the position of equilibrium must be shifted to the right. According to Le Chatelier's principle, decreasing the temperature will shift the position of equilibrium to the right. The temperature must be maintained at a level that is low enough to continue the forward reaction. This reaction is carried out at a temperature of 250 °C using the catalyst $Cu\text{-}ZnO\text{-}Al_2O_3$.

Additionally, according to Le Chatelier's principle, increasing the pressure will also shift the equilibrium to form more moles of methanol.

REVIEW QUESTIONS

(1) Hydrogen and bromine reversibly react as $H_2\,(g) + Br_2\,(g) \rightleftharpoons 2HBr\,(g)$.
   (a) Which of the following will favour the formation of more hydrogen bromide?
      (i) more hydrogen is added (ii) bromine is removed (iii) hydrogen bromide is removed as it forms
   (b) Explain why changing the pressure does not affect the amount of product produced in this equilibrium.

(2) Ammonia is prepared from nitrogen and hydrogen. The heat evolved in the reaction is 29 kJ mol^{-1}. The reaction is reversible and reaches equilibrium.
   (a) Write the thermochemical equation for this reaction.
   (b) Is the forward reaction endothermic or exothermic?
   (c) Explain why the ammonia yield (i) increases with increasing pressure and (ii) decreases with increasing temperature.

(3) How would you control the temperature and pressure to obtain more HCl in the given equilibrium? $2Cl_2\,(g) + 2H_2O\,(g) \rightleftharpoons 4HCl\,(g) + O_2\,(g) \qquad \Delta H = (+)$

4.3 EQUILIBRIUM CONSTANTS

In 1864, two Norwegian chemists proposed the ***law of mass action*** as a general description of the equilibrium condition. It is a quantitative law for predicting the amounts of reactants and products when a reaction reaches a state of dynamic equilibrium. According to the law of mass action, for a reversible reaction (in a closed system) at equilibrium and a constant temperature, the ratio between the concentration of reactants and products is constant.

(a) Deriving Equilibrium Constants

The equilibrium constant K_{eq}

Consider the general reaction occurring in the solution.

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

A and B are the reactants, C and D are the products while a, b, c, and d are the stoichiometric coefficients of the respective reactants and products. The rate of the forward reaction is directly proportional to the concentration of the reactants raised to a power equal to their coefficients. This can be shown using the following expressions:

$$\text{Rate of forward reaction} \propto [A]^a\,[B]^b$$

$$\text{Rate of forward reaction} = k_f\,[A]^a\,[B]^b$$

where k_f represents the rate constant for the forward reaction.

Similarly, the rate of the reverse reaction is directly proportional to the concentration of the products raised to a power equal to its coefficients. That is,

$$\text{Rate of reverse reaction} \propto [C]^c\,[D]^d$$

$$\text{Rate of reverse reaction} = k_r\,[C]^c\,[D]^d$$

where k_r represents the rate constant for the reverse reaction.

At equilibrium, the rates of forward and reverse reactions are equal.

$$\therefore\ k_f\,[A]^a\,[B]^b = k_r\,[C]^c\,[D]^d$$

$$\frac{k_f}{k_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Since $\frac{k_f}{k_r} = K_{eq}$, $$K_{eq} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

This ratio is called the equilibrium constant, K_{eq}. It is a characteristic numerical value of the ratio of product concentrations to reactant concentrations, with each concentration raised to the power corresponding to its coefficient in the balanced chemical equation. The value of K_{eq} is constant only at a specified temperature; that is, each chemical reaction has its own characteristic K_{eq}.

The equilibrium constant provides how far a reaction has gone towards completion before it reaches equilibrium. The units of equilibrium constant depend on the form of the equilibrium expression. Pure solids or liquids are excluded from the equilibrium expression because their concentrations remain constant throughout the reaction.

The equilibrium constant can describe whether the reaction tends to have a higher concentration of products or reactants at equilibrium.

If the K_{eq} value is large ($K_{eq} >> 1$), the equilibrium lies to the right and there are more products than reactants.

If the K_{eq} value is small ($K_{eq} << 1$), the equilibrium lies to the left and there are more reactants than products.

If the K_{eq} value is equal to one ($K_{eq} = 1$), both reactants and products are equally favoured at equilibrium and the concentration of reactants and products will be equal.

The equilibrium constant K_c

If molar concentrations are used, the equilibrium constant can be expressed as below.

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The equilibrium constant K_p

For equilibrium that involves gases, pressure can be used instead of concentration. Then, the equilibrium constant K_p can be given as the ratio of the partial pressures of products and reactants. The equilibrium constant is written as below.

$$K_p = \frac{p_C^c\,p_D^d}{p_A^a\,p_B^b}$$

Both K_p and K_c can be applied for the gaseous reactions.

(b) Equilibrium Constants for Homogeneous and Heterogeneous Equilibria

The relationship between the products and reactants of a homogeneous or heterogeneous reaction at equilibrium is shown by the equilibrium constant, K_{eq}.

Equilibrium constant for the homogeneous equilibrium

For a homogeneous equilibrium, e.g., $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$, the equilibrium constant can be expressed as below.

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

Equilibrium constant for the heterogeneous equilibrium

In many equilibrium systems, the substances involved are not all in the same phase. An example of a liquid-vapour heterogeneous equilibrium state is the equilibrium between ethanol (l) and ethanol (g) in a closed flask.

$$C_2H_5OH\ (l) \rightleftharpoons C_2H_5OH\ (g)$$

At a given temperature, the equilibrium constant expression becomes $K_{eq} = [C_2H_5OH\ (g)]$. Because ethanol is a pure liquid, its concentration is constant at a given temperature.

The equilibrium for the sublimation of iodine crystals is an example of the solid-vapour heterogeneous equilibrium state.

$$I_2\ (s) \rightleftharpoons I_2\ (g)$$

At a given temperature, the equilibrium constant expression becomes $K_{eq} = [I_2\ (g)]$. The equilibrium depends only on the concentration of gaseous iodine in the system.

Example 6: Write the equilibrium constant expression for the reaction in which ammonia gas is produced from hydrogen and nitrogen.

Solution:

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$$

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Example 7: Write expressions for K_c and K_p if applicable, for the given reversible reaction at equilibrium.

$$HF\ (aq) \rightleftharpoons H^+\ (aq) + F^-\ (aq)$$

Solution: The given reaction is a reaction occurring in the solution. There is no gas present and K_p is not applied.

$$K_c = \frac{[H^+][F^-]}{[HF]}$$

Example 8: Write the equilibrium constant expression (K_p) for the given reversible reaction at equilibrium.

$$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$$

Solution:

$$K_p = \frac{p^2_{SO_3}}{p^2_{SO_2} p_{O_2}}$$

Example 9: Write the equilibrium constant expression for the decomposition of baking soda (sodium hydrogen carbonate).

$$2NaHCO_3\ (s) \rightleftharpoons Na_2CO_3\ (s) + CO_2\ (g) + H_2O\ (g)$$

Solution:

$$K_{eq} = [CO_2][H_2O]$$

(c) Calculation Concerning the Equilibrium Constants

The numerical value of the equilibrium constant is determined by measuring the concentration of each substance involved in a chemical reaction at equilibrium. When equilibrium is established, the concentration of each substance is determined experimentally, and the equilibrium constants are calculated from the ratio of the product concentrations to reactant concentrations.

Conversely, the equilibrium concentration of any substance involved in a reaction can be calculated by using the equilibrium constant. An example that shows how to calculate the value of the equilibrium constant is given below.

Example 10: The equilibrium $2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$ was investigated at 230 °C. In one experiment, the concentrations of NO, O_2, NO_2 were respectively found to be 0.542 mol dm^{-3}, 0.127 mol dm^{-3}, and 0.059 mol dm^{-3} at equilibrium. Calculate the equilibrium constant (K_c) of the reaction and identify the direction of equilibrium.

Solution:

$$K_c = \frac{[NO_2]^2}{[NO]^2\,[O_2]}$$

$$= \frac{(0.059)^2}{(0.542)^2\,(0.127)}$$

$K_c = 0.093\ dm^3\ mol^{-1}$

Since the K_c value is small ($K_c << 1$), the equilibrium lies to the left and the reaction mixture contains mostly reactants (NO and O_2).

Note: The equilibrium constant expression can be useful in another way. Knowing the constant expression, a chemist can calculate the equilibrium concentration of any substance involved in a reaction if the concentrations of all other reactants and products are known.

Example 11: Hydrogen sulphide gas decomposes to form hydrogen and diatomic sulphur gaseous molecules, S_2 at 1405 K. The equilibrium constant for the reaction is 2.270×10^{-3}. The concentration of H_2 can be calculated, if $[S_2] = 0.054$ mol dm^{-3} and $[H_2S] = 0.184$ mol dm^{-3}. How much of the concentration of hydrogen gas would be produced?

Solution:

$$2H_2S\,(g) \rightleftharpoons 2H_2\,(g) + S_2\,(g)$$

0.184 mol dm^{-3} ? 0.0540 mol dm^{-3}

$$K_{eq} = \frac{[H_2]^2\,[S_2]}{[H_2S]^2}$$

$$[H_2]^2 = \frac{K_{eq} \times [H_2S]^2}{[S_2]}$$

$$[H_2]^2 = \frac{2.270 \times 10^{-3} \times (0.184)^2}{0.054}$$

$$= 0.1423 \times 10^{-2}$$

$$[H_2] = \sqrt{0.1423 \times 10^{-2}}$$

$= 0.0377\ mol\ dm^{-3}$

REVIEW QUESTIONS

(1) What is the difference between K_p and K_c?

(2) Write the expressions for K_c and K_p if applicable, for the following reversible reactions at equilibrium:

(i) $CH_3COOC_2H_5\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COOH\,(aq) + C_2H_5OH\,(aq)$

(ii) $Cd^{2+}\,(aq) + 4Br^-\,(aq) \rightleftharpoons CdBr_4^{2-}\,(aq)$

(iii) $CH_4\,(g) + 2H_2S\,(g) \rightleftharpoons CS_2\,(l) + 4H_2\,(g)$

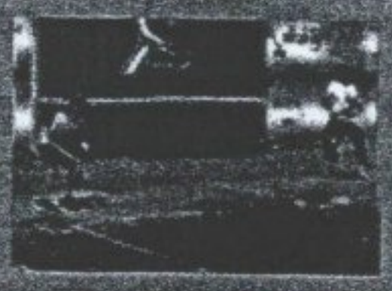
(3) At a certain temperature, $K_{eq} = 10.5$ for the equilibrium $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
   (a) calculate the concentration of CH_3OH in an equilibrium mixture containing 0.0661 mol dm^{-3} of H_2 and 3.85 mol dm^{-3} of CO.
   (b) calculate the concentration of H_2 in an equilibrium mixture containing 1.09 mol dm^{-3} of CO and 0.325 mol dm^{-3} of CH_3OH.

Key Term

- **Equilibrium constant** is a ratio that expresses the relationship between the amounts of products and reactants present at equilibrium in a reversible chemical reaction at a given temperature.

Chemistry in Society

- When the hot air and cold air are entering the room at the same time the overall temperature of the room does not change at all.
- In a championship match, the muscles of tennis players need extra oxygen. The transfer of O_2 from the lungs to the blood and then to the muscle tissues depends on the chemical equilibrium between oxygen and haemoglobin.



- When running on a treadmill, the person is in constant motion or dynamic equilibrium. The person is moving forwards, simultaneously, and the treadmill is moving backwards at the same rate.

EXERCISES

Q 1 to Q 3 (Understanding)

1. For each of the following, say whether the statement is TRUE or FALSE. If the statement is FALSE, correct it.
   (a) Reversible reactions can proceed in the forward direction only.
   (b) An increase in temperature would favour the exothermic reaction.
   (c) The reaction is completely stopped at equilibrium.
   (d) The effect of changing the pressure on a reaction involving liquids is negligible.
   (e) The equilibrium does not depend on the initial concentration of reactants.

2. Fill in the blanks with a suitable word or phrase or symbol as necessary.
   (a) The system of reaction in which no reactant leaves the reaction mixture is termed as _____.
   (b) The reaction in which product cannot turn back into reactant is known as _____ reaction.
   (c) If the K_{eq} value is _____ than 1, the equilibrium lies to the right and there are more products than reactants.
   (d) At equilibrium, the rate of forward and _____ reactions become equal.
   (e) A _____ reaction is a reaction that can proceed in both directions.

3. Choose the correct one from each of the following:
   (a) The reversible reaction is carried out in (an open system only, a closed system only, both open and closed systems) to achieve dynamic equilibrium.
   (b) Due to the high concentration of reactants, the rate of the forward reaction is (slow, moderate, fast).
   (c) A decrease in temperature would favour (the endothermic reaction, the exothermic reaction, none of these reactions).
   (d) The reaction proceeding to the right is called a (forward, reverse, reversible) reaction.
   (e) The composition of equilibrium mixture does not change by the (catalyst, temperature, concentration).

Q 4 to Q 11 (Critical Thinking and Problem Solving)

4. Use this chemical reaction; $CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$ Explain what happens to the position of equilibrium when (i) some $CH_3COOH\ (l)$ is removed and (ii) more $C_2H_5OH\ (l)$ is added.

5. Predict the effect of decreasing the pressure on each of the following equilibria:
   (a) $2H_2O\ (g) + N_2\ (g) \rightleftharpoons 2H_2\ (g) + 2NO\ (g)$ (b) $CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g)$

6. How would you change the temperature and pressure in the following equilibrium to get the highest quantity of $CaCO_3\ (s)$ on the right-hand side?
   $$CaO\ (s) + CO_2\ (g) \rightleftharpoons CaCO_3\ (s) \quad \Delta H = (+)$$

7. For the reaction $2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$ $\Delta H = (-)$, to maximise the yield of SO_3,
   (i) would you keep the pressure high or low on the equilibrium?
   (ii) would you keep the temperature high or low during the reaction?
   (iii) would the yield of SO_3 change if a catalyst was added?

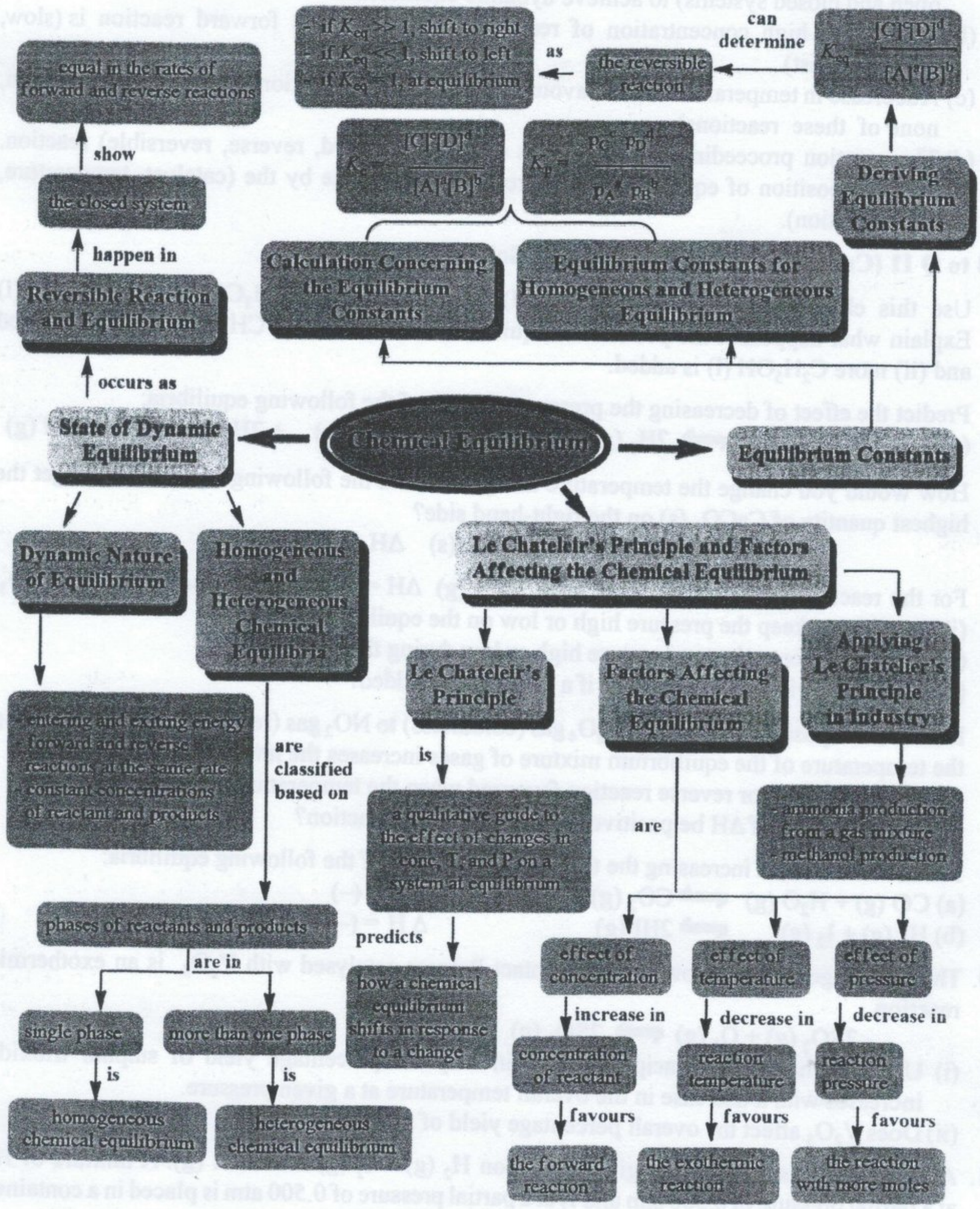
8. In the decomposition reaction of N_2O_4 gas (colourless) to NO_2 gas (reddish-brown), increasing the temperature of the equilibrium mixture of gases increases the intensity of the colour.
   (i) Is the forward or reverse reaction favoured when the temperature is increased?
   (ii) Will the sign of ΔH be positive or negative in this reaction?

9. Predict the effect of increasing the temperature on each of the following equilibria:
   (a) $CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$ $\Delta H = (-)$
   (b) $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$ $\Delta H = (-)$

10. The first stage (given below) of the Contact Process catalysed with V_2O_5 is an exothermic reaction.
    $$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$$
    (i) Use Le Chatelier's principle to explain why the percentage yield of sulphur trioxide increases with a decrease in the overall temperature at a given pressure.
    (ii) Does V_2O_5 affect the overall percentage yield of sulphur trioxide?

11. At 430 °C, K_p is 54.3 for the given reaction $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$. A mixture of H_2 at a partial pressure of 0.500 atm and I_2 at a partial pressure of 0.500 atm is placed in a container at 430 °C. Calculate the equilibrium partial pressure of HI.

CHAPTER REVIEW
(Concept Map)



CHAPTER 5

ACID-BASE REACTIONS

Acid-base reactions are essential in the fields of chemistry such as biochemistry, agricultural chemistry, industrial chemistry, and environmental chemistry. When an acid and a base react, they neutralise each other to form a salt. It is important to realise that these neutralisation reactions are important in domestic uses, biological uses, and industrial uses. Antacids such as aluminium hydroxide and magnesium hydroxide (magnesia) are taken when a person has a stomach ulcer. Calcium oxide (quicklime) is applied to acidic soil to neutralise it. Limewater can be used to absorb harmful sulphur dioxide released from the power station. We have learned that pH is a measure of the acidity or alkalinity of the solution. In some processes, it is required to keep the pH values constant. To resist the changes in pH values, buffering action is needed. This is important for processes and reactions which require specific and stable pH ranges. Buffering in the blood is crucial to our survival. The pH of blood must be kept constant for normal body functions to work. Buffers are used in many household items. For instance, buffers are used in shampoos to stop skin irritation caused by ingredients like sodium hydroxide.

Previously, we have learned the properties of acids and bases, as well as salts, which are products of reactions between acids and bases (neutralisation reactions). Early known characteristics of acids and bases include that they are the main chemicals in all the chemistry that occurs in water. Here, we will study how acids and bases are related to water. This chapter also focuses on the further idea of the chemistry of acid-base reactions, ionic equilibria and the buffering action of the acids or bases.

Milk of magnesia

Quicklime

Buffer solutions

Shampoo

Learning Outcomes

After completing this chapter, students will be able to:

- describe the Arrhenius, Brønsted-Lowry, and Lewis acid-base theories;
- explain the conjugate acid-base pairs;
- discuss the ionic product constant for the autoionisation of water and define pH as a measure of acidity and alkalinity;
- deduce the expressions for the dissociation constants of weak acids and weak bases, and solve problems for pH, pOH, $[H^+]$ and $[OH^-]$;
- predict whether a salt solution will be acidic, basic, or neutral;
- explain the buffer solutions and perform the calculations related to buffer solutions.

5.1 THEORIES OF ACIDS AND BASES

Definitions of acid and base have changed dramatically as scientists have learned more about them. Svante Arrhenius, Johannes Nicolaus Brønsted, Thomas Martin Lowry, and Gilbert Newton Lewis made significant contributions to the current understanding of definitions of acids and bases.

(a) Arrhenius Theory

The first person to define acids and bases was the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry, 1903). He proposed that acids are any substances that dissociate to produce hydrogen ions (H^+) when they dissolve in water. An example of an **Arrhenius acid** is hydrochloric acid. Strong acids such as hydrochloric acid completely ionise in water, whereas weak acids such as ethanoic acid only partially ionise.

e.g., $HCl\,(aq) \longrightarrow H^+\,(aq) + Cl^-\,(aq)$

$CH_3COOH\,(aq) \rightleftharpoons H^+\,(aq) + CH_3COO^-\,(aq)$

Bases are any substances that dissociate to produce hydroxide ions (OH^-) when they dissolve in water. An example of an **Arrhenius base** is sodium hydroxide. Strong bases such as sodium hydroxide completely ionise in an aqueous solution, whereas weak bases such as ammonium hydroxide only partially ionise.

e.g., $NaOH\,(aq) \longrightarrow Na^+\,(aq) + OH^-\,(aq)$

$NH_4OH\,(aq) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$

Arrhenius theory has some weak points, one of which is that its application is limited to aqueous solutions. It is unable to account for the acidic properties of CO_2, SO_2, SO_3, etc., which do not have hydrogen, and the basic properties of CaO, MgO, etc., which do not have hydroxyl groups.

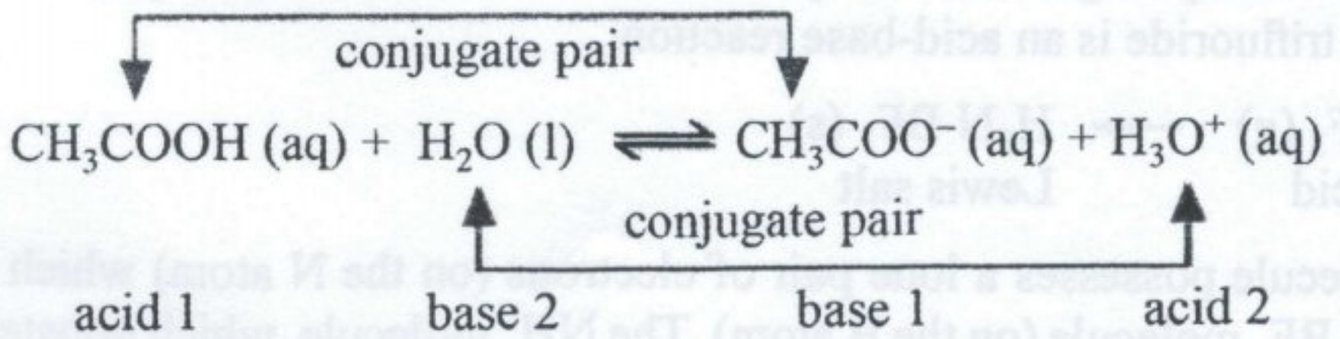
(b) Brønsted-Lowry Theory

The Danish chemist Johannes Nicolaus Brønsted (1879–1947) and the English chemist Thomas Martin Lowry (1874–1936) independently proposed a new theory, called the Brønsted-Lowry theory.

Acids are proton donors and bases are proton acceptors. This definition applies to all solvents, not only to aqueous solutions. An extension of the Brønsted-Lowry definition of acids and bases is the concept of the **conjugate acid-base pair**, which consists of either an acid and its **conjugate base** or a base and its **conjugate acid**.

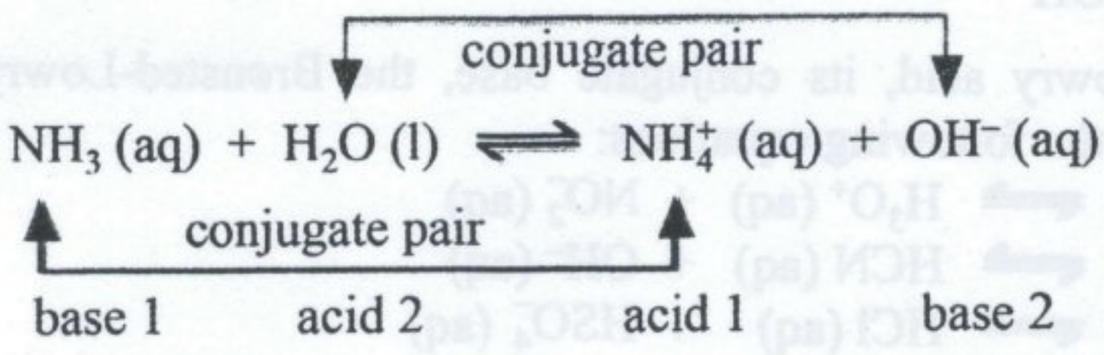
The conjugate base of a **Brønsted-Lowry acid** is the species that remains when one proton has been removed from the acid. Conversely, a conjugate acid results from the addition of a proton to **a Brønsted-Lowry base**. Every Brønsted-Lowry acid and base has a corresponding conjugate base and conjugate acid. A strong acid has a weak conjugate base and a strong base has a weak conjugate acid, and vice versa.

For example, when ethanoic acid (CH_3COOH) dissolves in water, the following equilibrium is established:



CH_3COOH molecule donates a proton to water forming CH_3COO^- ion (ethanoate ion). Therefore, CH_3COOH is classified as a Brønsted-Lowry acid (acid 1), and CH_3COO^- ion is its conjugate base (base 1). On the other hand, the H_2O molecule accepts that proton forming H_3O^+ ion (hydronium ion). Therefore, the H_2O molecule acts as a base (base 2), and its conjugate acid is H_3O^+ ion (acid 2). CH_3COOH, which loses a proton with difficulty, is a weak acid and its conjugate base CH_3COO^- ion is a strong base.

When the ammonia molecule dissolves in water the following equilibrium is established:



NH_3 molecule accepts a proton from water forming NH_4^+ ion. Thus, NH_3 is a Brønsted-Lowry base (base 1) and NH_4^+ ion is its conjugate acid (acid 1). H_2O molecule donates a proton forming OH^- ion. Thus, the H_2O molecule acts as an acid (acid 2), and its conjugate base is OH^- ion (base 2). NH_3 is a weak base and its conjugate acid NH_4^+ ion is a strong acid.

The Brønsted-Lowry theory fails to explain the reaction between acidic oxides (CO_2, SO_2, and SO_3) and basic oxides (BaO, CaO, and Na_2O) because there is no proton transfer. Substances such as BF_3, $AlCl_3$ etc., do not have any hydrogen and thus cannot give a proton but are known to behave as acids. It does not explain the reactions occurring in the non-protonic solvents like $COCl_2$, SO_2, N_2O_4, etc.

Example 1: (a) What are (i) the conjugate bases for the acids HNO_2, HF, H_2S, and HSO_4^- and (ii) the conjugate acids for the bases NH_2^-, NH_3, and CH_3COO^-?

Solution:

(i) For the acids, HNO_2, HF, H_2S, and HSO_4^-, the corresponding conjugate bases are - NO_2^-, F^-, HS^-, and SO_4^{2-}, respectively.

(ii) For the bases, NH_2^-, NH_3, and CH_3COO^-, the corresponding conjugate acids are - NH_3, NH_4^+, and CH_3COOH, respectively.

(c) Lewis Theory

In 1932, American chemist Gilbert Newton Lewis (1875–1946) proposed that bases are species that can donate an electron pair, and acids are species that can accept an electron pair. The Lewis concept is significant since it is more general than any of the other definitions which define

only the involvement of hydrogen ions or protons as an acid. For example, the reaction of ammonia with boron trifluoride is an acid-base reaction.

$$\underset{\text{base}}{H_3N:(g)} + \underset{\text{acid}}{BF_3(g)} \longrightarrow \underset{\text{Lewis salt}}{H_3N\text{-}BF_3(s)}$$

The NH_3 molecule possesses a lone pair of electrons (on the N atom) which is shared by the electron-deficient BF_3 molecule (on the B atom). The NH_3 molecule, which donates an electron pair, behaves as a **Lewis base**. The BF_3 molecule, which accepts an electron pair, behaves as a **Lewis acid**.

REVIEW QUESTIONS

(1) Identify Lewis acids and Brønsted-Lowry acids from the following molecules and ions and explain your answers.
BF_3, H^+, HF, $AlCl_3$, HCOOH

(2) Identify the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base and its conjugate acid in each of the following equations:

(a) $HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$

(b) $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$

(c) $H_2SO_4(aq) + Cl^-(aq) \rightleftharpoons HCl(aq) + HSO_4^-(aq)$

(3) HCN can act as both Arrhenius acid and Brønsted-Lowry acid. Explain why.

Key Terms

- **Arrhenius acid** is any substance that dissociates to produce hydrogen ions (H^+) when it dissolves in water.
- **Arrhenius base** is any substance that dissociates to produce hydroxide ions (OH^-) when it dissolves in water.
- **Brønsted-Lowry acid** is any substance that can donate a proton.
- **Brønsted-Lowry base** is any substance that can accept a proton.
- **Conjugate acid** is a species that forms when a base gains a proton.
- **Conjugate base** is a species that forms when an acid loses a proton.
- **Conjugate acid-base pair** is an acid-base pair that consists of either an acid and its conjugate base or a base and its conjugate acid.
- **Lewis acid** is any substance that can accept an electron pair.
- **Lewis base** is any substance that can donate an electron pair.

5.2 IONIC DISSOCIATION OF WATER AND pH

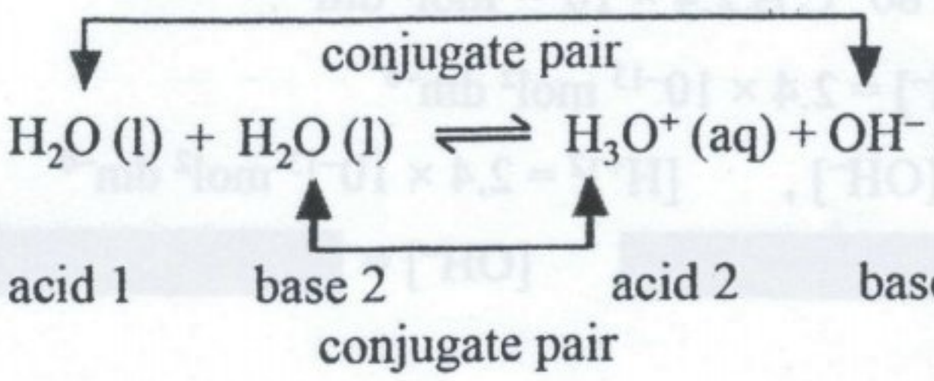
When ionic compounds dissolve in water, dissociation reactions occur. Water can also dissociate into hydrogen and hydroxide ions, and the process is known as autoionisation. In pure water, very little dissociation takes place. The number of hydrogen ions that water will receive, determines the pH, which is related to hydrogen ion concentration.

(a) Acid-base Behaviour of Water

The capacity of water to function as an acid or a base is one of its unique characteristics. Water can show both acidic and basic behaviour. In reactions with acids like HCl and CH_3COOH, water acts as a base, and in reactions with bases like NH_3, it acts as an acid. Although water is a very weak electrolyte and a poor conductor of electricity, it undergoes ionisation to a small extent.

$$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

This reaction is called the **autoionisation of water**. To describe the acid-base properties of water in the Brønsted-Lowry framework, the autoionisation can be expressed as follows:



In pure water, one H_2O molecule donates a proton and acts as an acid, and another water molecule accepts a proton and acts as a base at the same time. The acid-base conjugate pairs are (1) H_2O (acid) and OH^- (base) and (2) H_3O^+ (acid) and H_2O (base).

Having both proton-accepting (protophilic) and proton-donating (protogenic) properties, water is called an **amphiprotic molecule**.

(b) The Ionic Product of Water

Pure water undergoes ionisation to a very slight extent. The ionisation of water can be expressed as follows:

$$H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

Generally, the following equation is used to write an equilibrium expression for this reaction:

$$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

Therefore, $$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K\,[H_2O] = [H^+]\,[OH^-]$$

Since water ionises to a very slight extent, the equilibrium concentration of undissociated water does not differ appreciably from the original concentration. The concentration of water $[H_2O]$ remains constant.

Thus, $K_w = [H^+][OH^-]$, where $K_w = K\,[H_2O]$. K_w is called the **ionic product of water** which is the product of the molar concentrations of H^+ and OH^- ions at a particular temperature.

From the measurement of the electrical conductance of pure water, it was found that the concentration of ionised ion was 1.0×10^{-7} mol dm^{-3}. In pure water, the concentration of H^+ ion is always equal to the concentration of OH^- ion.

$[H^+] = [OH^-] = 1.0 \times 10^{-7}$ mol dm^{-3} at 25 °C (298 K)

Substituting these concentrations into the K_w expression gives as

$$K_w = [H^+][OH^-] = (1.0 \times 10^{-7}\ \text{mol dm}^{-3})\,(1.0 \times 10^{-7}\ \text{mol dm}^{-3})$$
$$= 1.0 \times 10^{-14}\ \text{mol}^2\,\text{dm}^{-6} \text{ at 25 °C (298 K)}$$

This expression is also valid for dilute aqueous solutions at 25 °C (298 K). It gives a simple relationship between H^+ and OH^- concentrations in all dilute aqueous solutions. If the individual concentration of hydrogen ions and hydroxide ions in an aqueous solution is equal to 1.0×10^{-7} mol dm^{-3} at 25 °C (298 K), the solution is called a **neutral aqueous solution**.

Since the process of autoionisation is endothermic, the concentrations of hydrogen ions and hydroxide ions increase with temperature. For instance, at 100 °C (373 K), the value for K_w is approximately 5.6×10^{-13} mol^2 dm^{-6}, which is roughly 50 times greater than the value at 25 °C (298 K). At different temperatures, the K_w has different values.

Example 2: Calculate the concentrations of hydrogen and hydroxide ions in pure water at 80 °C. The ionic product of water at 80 °C is 2.4×10^{-13} mol^2 dm^{-6}.

Solution: $K_w = [H^+][OH^-] = 2.4 \times 10^{-13}$ mol^2 dm^{-6}

Since $[H^+] = [OH^-]$, $[H^+]^2 = 2.4 \times 10^{-13}$ mol^2 dm^{-6}

$[H^+] =$ 4.9×10^{-7} mol dm^{-3}, $[OH^-] =$ 4.9×10^{-7} mol dm^{-3}

(c) The pH and pOH

Most concentrations of hydronium ions are very small and difficult to express. In 1909, Soren P. Sorenson (1868-1939), a Danish biochemist proposed the potency of the hydrogen (pH) scale, a scale ranging from 0 to 14 pH that is used to measure the acidity or alkalinity of a solution. The **pH** and **pOH** scales express the acidity and alkalinity of dilute aqueous solutions.

The negative logarithm to base 10 of the molar concentration of hydrogen ions is used to calculate the pH. A mathematical expression is given as

$$pH = -\log [H_3O^+] \text{ or simply } pH = -\log [H^+]$$

To calculate the H^+ ion concentration of the solution of a given pH value, it is needed to take the antilogarithm of the above expression as follows:

$$[H^+] = 10^{-pH} = \text{antilog}(-pH)$$

Similarly, pOH is the negative logarithm to base 10 of the molar concentration of the hydroxide ions. A mathematical expression is shown below.

$$pOH = -\log [OH^-] \quad \text{and} \quad [OH^-] = 10^{-pOH} = \text{antilog}(-pOH)$$

The relation between the concentrations of these two ions expressed as p-functions (pH and pOH) is easily derived from the K_w expression.

$$K_w = [H^+][OH^-]$$

$$-\log K_w = -\log [H^+][OH^-] = \{-\log [H^+]\} + \{-\log[OH^-]\}$$

$$pK_w = pH + pOH$$

At 298 K, the value of K_w is 1.0×10^{-14} mol^2 dm^{-6}, and so,

$$pH + pOH = pK_w = -\log (1.0 \times 10^{-14})$$

$$pH + pOH = 14$$

Acids have pH values of less than 7. For acids, the smaller the pH value (the higher the concentration of H^+ ions), the stronger the acid is. Alkalis have pH values greater than 7. For alkalis, the larger the pH value (the higher the concentration of OH^- ions), the stronger the alkali is. Neutral solutions have a pH value of 7. Figure 5.1 shows the pH scale diagram. The solutions of different pH values develop their respective different colours with the use of a Universal indicator (in the form of paper or solution).

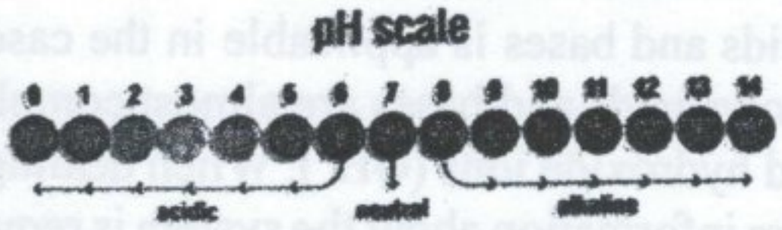


Figure 5.1 pH Scale Diagram with Corresponding Acidic and Alkaline Solutions

Example 3: What is the pH of grapefruit juice with a hydrogen ion concentration of 6.5×10^{-4} mol dm^{-3}?

Solution: $[H^+] = 6.5 \times 10^{-4}$ mol dm^{-3}

$pH = -\log [H^+] = -\log\ 6.5 \times 10^{-4} = -0.81 + 4 =$ 3.19

Example 4: Human blood pH normally ranges from 7.35 to 7.45. Calculate the hydrogen and hydroxide ion concentrations in human blood with a pH of 7.4.

Solution: $pH = -\log [H^+] = 7.4$

$\log [H^+] = -7.4$

$[H^+] = \text{antilog}\ (-7.4) =$ 3.98×10^{-8} mol dm^{-3}

$[H^+][OH^-] = 1.0 \times 10^{-14}$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = \frac{1.0 \times 10^{-14}}{3.98 \times 10^{-8}} =$$ 2.51×10^{-7} mol dm^{-3}

REVIEW QUESTIONS

(1) The ionisation constant for water (K_w) is 2.9×10^{-14} mol^2 dm^{-6} at 40 °C. Calculate $[H^+]$, $[OH^-]$ and pH for pure water at 40 °C.

(2) Acid rain is a matter of serious concern because most fish species die in waters with a pH less than 4.5 . Calculate the $[H^+]$ in a lake having a pH of 4.5.

(3) Calculate the concentration of OH^- ions of the runoff from a coal mine with H^+ ion concentration of 1.2×10^{-4} mol dm^{-3}. Is the solution acidic, basic, or neutral?

Key Terms

- **Autoionisation of water** is a reaction between two water molecules yielding hydronium and hydroxide ions.
- **Amphiprotic molecule** is one which can have both proton-accepting (protophilic) and proton-donating (protogenic) properties.
- **Ionic product of water** is the equilibrium constant for the autoionisation of water which is the product of the molar concentrations of H^+ and OH^- ions at a particular temperature.
- **Neutral aqueous solution** is one in which the concentrations of hydrogen ions and hydroxide ions are equal at the value of 1.0×10^{-7} mol dm^{-3} at 25 °C (298 K) (pH = 7).

- **pH** is defined as the negative logarithm to base 10 of the molar concentration of the hydrogen ions.
- **pOH** is defined as the negative logarithm to base 10 of the molar concentration of the hydroxide ions.

5.3 IONISATION OF ACIDS AND BASES

Arrhenius's concept of acids and bases is applicable in the case of ionisation of acids and bases. In an aqueous solution, strong acids and bases are almost completely dissociated (ionised), producing hydrogen ions (H^+) and hydroxide ions (OH^-). When dealing with aqueous solutions of weak acids or bases, however, more information about the system is required as they undergo partial dissociation. Acids and bases differ greatly based on their strengths. The strengths of acids and bases can be ranked by the extent to which they ionise in aqueous solutions.

(a) Strong Acids and Weak Acids

Strong acids are strong electrolytes that completely ionise in water. Most of the strong acids are inorganic acids. Examples are hydrochloric acid (HCl), nitric acid (HNO_3), perchloric acid ($HClO_4$), and sulphuric acid (H_2SO_4). When strong acids are dissolved in water, the following reactions take place:

e.g., $HCl\,(aq) \longrightarrow H^+\,(aq) + Cl^-\,(aq)$

$HClO_4\,(aq) \longrightarrow H^+\,(aq) + ClO_4^-\,(aq)$

$H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4^-\,(aq)$ } 2 steps

$HSO_4^-\,(aq) \rightleftharpoons H^+\,(aq) + SO_4^{2-}\,(aq)$

(HSO_4^- is still acidic since it has a replaceable hydrogen atom.)

Most organic acids are **weak acids**. Weak acids are weak electrolytes that partially ionise only to a limited extent in water. Some examples of weak acids are hydrofluoric acid (HF), hypochlorous acid (HOCl), ethanoic acid (CH_3COOH), and methanoic acid (HCOOH).

e.g., $HF\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + F^-\,(aq)$

$HCOOH\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCOO^-\,(aq)$

Basicity of an acid

The **basicity** of an acid may be defined as the number of H^+ ions that one molecule of acid can produce. For example, the basicity of hydrochloric acid is one because each molecule can give only one H^+ ion. The basicity of sulphuric acid is two since each molecule can provide two H^+ ions.

e.g., $HCl\,(aq) \longrightarrow H^+\,(aq) + Cl^-\,(aq)$

$H_2SO_4\,(aq) \longrightarrow 2H^+\,(aq) + SO_4^{2-}\,(aq)$

Thus, the number of hydrogen ions that one molecule of acid can produce is the basicity of acid.

Acids that donate a maximum of one, two, or three protons are called monoprotic acids (HCl, CH_3COOH), diprotic acids (H_2SO_4, H_2CO_3), or triprotic acids (H_3PO_4), respectively, and are also called monobasic acids, dibasic acids, or tribasic acids, respectively.

Some strong and weak acids are shown in Table 5.1.

Table 5.1 Some Common Strong and Weak Acids

Strong acids		Weak acids	
$HClO_4$	perchloric acid	HF	hydrofluoric acid
HI	hydroiodic acid	HNO_2	nitrous acid
HBr	hydrobromic acid	HCOOH	methanoic acid
HCl	hydrochloric acid	CH_3COOH	ethanoic acid
H_2SO_4	sulphuric acid	H_2CO_3	carbonic acid
HNO_3	nitric acid	HCN	hydrocyanic acid

Example 5: Calculate $[H^+]$, $[OH^-]$, and pH for a 0.02 mol dm^{-3} HNO_3 solution.

Solution:

$$HNO_3\ (aq) \longrightarrow H^+\ (aq) + NO_3^-\ (aq)$$

0.02 mol dm^{-3} 0.02 mol dm^{-3}

$[H^+] =$ 0.02 mol dm^{-3}

$[H^+]\,[OH^-] = K_w = 1 \times 10^{-14}$ mol^2 dm^{-6}

$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = \frac{1.0 \times 10^{-14}}{0.02} = 5 \times 10^{-13} \text{ mol dm}^{-3}$$

$$pH = -\log [H^+] = -\log 0.02 = -\log (2 \times 10^{-2})$$

$$= -0.301 + 2 = 1.699$$

(b) Strong Bases and Weak Bases

In common usage, the word "alkali" and "base" are interchangeable. A base is a substance that reacts with an acid whereas an alkali is a base that is soluble in water. Hydroxides of alkali metals (Li, Na, K) and certain alkaline earth metals (Ca, Sr, Ba) are **strong bases**. Like strong acids, strong bases are strong electrolytes that ionise completely in water. The ionisation reactions of some strong bases are shown below.

$$NaOH\ (aq) \longrightarrow Na^+\ (aq) + OH^-\ (aq)$$
$$Ba(OH)_2\ (aq) \longrightarrow Ba^{2+}\ (aq) + 2OH^-\ (aq)$$

Weak bases, like weak acids, are weak electrolytes that ionise to a very limited extent in water. Ammonia, aniline, methylamine, and pyridine are examples of weak bases.

e.g., $NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$

Acidity of a base

The **acidity** of a base is measured by the number of molecules of a **monoprotic acid**, like HCl, which will neutralise one molecule of the base. For example, one molecule of NaOH neutralises one molecule of HCl and therefore has an acidity of one. $Ca(OH)_2$ has an acidity of two because it neutralises two molecules of HCl.

e.g., $NaOH\ (aq) + HCl\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (l)$
$Ca(OH)_2\ (aq) + 2HCl\ (aq) \longrightarrow CaCl_2\ (aq) + 2H_2O\ (l)$

Some strong and weak bases are shown in Table 5.2.

Table 5.2 Some Common Strong and Weak Bases

Strong bases		Weak bases	
LiOH	lithium hydroxide	NH_3	ammonia
NaOH	sodium hydroxide	CH_3NH_2	methylamine
KOH	potassium hydroxide	$(CH_3)_2NH$	dimethylamine
$Ca(OH)_2$	calcium hydroxide	$(CH_3)_3N$	trimethylamine
$Sr(OH)_2$	strontium hydroxide		
$Ba(OH)_2$	barium hydroxide		

Example 6: Calculate pH and pOH for 0.012 mol dm^{-3} of slaked lime, $Ca(OH)_2$ solution.

Solution: $Ca(OH)_2\,(aq) \longrightarrow Ca^{2+}\,(aq) + 2OH^-\,(aq)$

$0.012\ mol\ dm^{-3} \qquad 2 \times 0.012\ mol\ dm^{-3}$

$[OH^-] = 2 \times 0.012 = 0.024\ mol\ dm^{-3}$

$pOH = -\log [OH^-] = -\log 0.024 = -(-1.62) = 1.62$

$pH + pOH = 14$

$pH = 14 - pOH = 14 - 1.62 = 12.38$

(c) Relative Strengths of Acids and Bases

Acid dissociation constants

A strong acid completely ionises in water. The relative strengths of acids may be determined by measuring the acid ionisation constants, K_a, in aqueous solutions. Consider the reaction of a weak monoprotic acid HA.

$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$

or $HA\,(aq) \rightleftharpoons H^+\,(aq) + A^-\,(aq)$

The equation for the ionisation constant is expressed as $K_a = \dfrac{[H^+]\,[A^-]}{[HA]}$.

The strength of an acid is related to its degree of ionisation, the magnitude of which is reflected by the value of its **dissociation constant**, K_a (same as the ionisation constant for complete ionisation). The larger the K_a value of an acid, the greater its dissociation, the higher the concentrations of H^+ and the stronger is the acid. Thus, the dissociation constant of a stronger acid is greater than that of a weaker acid. The dissociation constants increase as the strength of the acids increases. For example, the strength of the following acids can be indicated by their acid dissociation constants:

$HNO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + NO_2^-\,(aq) \qquad K_a = 4.5 \times 10^{-4}$

$HSO_4^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + SO_4^{2-}\,(aq) \qquad K_a = 1.3 \times 10^{-2}$

$CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3COO^-\,(aq) \qquad K_a = 1.8 \times 10^{-5}$

The decreasing order of acid strength is $HSO_4^- > HNO_2 > CH_3COOH$.

The dissociation constant of a weak acid is sometimes expressed on a logarithmic scale, which for acid is denoted by the relation $pK_a = -\log K_a$. Small K_a values (corresponding to large pK_a) indicate weak acids. K_a and pK_a may be used to indicate their comparative acid strengths.

Example 7: Nicotinic acid is a weak organic acid that can be represented as HA.

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$

The equilibrium concentrations of a dilute solution of nicotinic acid at 298 K are given as, $[HA] = 0.049$ mol dm^{-3} and $[H_3O^+] = [A^-] = 8.4 \times 10^{-4}$ mol dm^{-3}. What are the K_a and pK_a values?

Solution: $HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$

or $HA\,(aq) \rightleftharpoons H^+\,(aq) + A^-\,(aq)$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} = \frac{8.4 \times 10^{-4} \times 8.4 \times 10^{-4}}{0.049} = 1.4 \times 10^{-5}$$

$$pK_a = -\log K_a = -\log 1.4 \times 10^{-5} = -0.146 + 5 = 4.854$$

Base dissociation constants

Similarly, the relative strengths of bases can be determined by measuring their **base dissociation constants**, K_b, in aqueous solutions. The higher the K_b value of a base, the greater its dissociation and the higher the concentrations of OH^- ions will be. The dissociation constants increase as the strength of the base increases. Consider the reaction of a base, B.

$$B\,(aq) + H_2O\,(l) \rightleftharpoons HB^+\,(aq) + OH^-\,(aq)$$

The equation for the dissociation constant is expressed as $K_b = \dfrac{[HB^+][OH^-]}{[B]}$.

The water is not included in the equilibrium expression as it is in such great excess, that the concentration of water does not change significantly with changes in the concentrations of other species.

The following data on base dissociation constants indicate the order of base strength.

$$CH_3COO^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COOH\,(aq) + OH^-\,(aq) \qquad K_b = 5.6 \times 10^{-10}$$
$$NO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons HNO_2\,(aq) + OH^-\,(aq) \qquad K_b = 2.2 \times 10^{-11}$$
$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq) \qquad K_b = 1.8 \times 10^{-5}$$

The decreasing order of base strength is $NH_3 > CH_3COO^- > NO_2^-$.

For a base, the dissociation constant is expressed on a logarithmic scale, which is denoted by the relation $pK_b = -\log K_b$. Small K_b values (corresponding to large pK_b) indicate weak bases. K_b and pK_b may be used to indicate their comparative base strengths.

Example 8: Use a 0.055 mol dm^{-3} solution of weak base ammonia having hydroxide ion concentration of 1.0×10^{-3} mol dm^{-3}, and calculate the K_b value.

Solution: $NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$

$$[OH^-] = [NH_4^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$$

The ionisation of the weak base is so small that the concentration of undissociated NH_3 molecule present at equilibrium is approximately the same as that of the original concentration.

Thus, $[NH_3] = 0.055$ mol dm^{-3}

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$K_b = \frac{(1.0 \times 10^{-3})(1.0 \times 10^{-3})}{0.055} = 1.82 \times 10^{-5}$$

REVIEW QUESTIONS

(1) The K_a values for ethanoic acid (CH_3COOH) and hydrofluoric acid (HF) are 1.8×10^{-5} and 7.2×10^{-4}, respectively. What are their pK_a values? Which one is stronger?
(2) Calculate the pH of an aqueous solution containing 7.3 g HCl per dm^3. (H = 1, Cl = 35.5)
(3) (a) What is the relationship between the strength of an acid and the numerical value of K_a?
(b) What is the relationship between the base strength and the value of pK_b?
(c) Given the following list of weak acids and their K_a values, arrange the acids in order of (i) increasing acid strength and (ii) increasing pK_a values.

HOCl ($K_a = 3.5 \times 10^{-8}$) ; HCN ($K_a = 4.9 \times 10^{-10}$) ; HNO_2 ($K_a = 4.5 \times 10^{-4}$)

Key Terms

- **Strong acids** are strong electrolytes that completely ionise in water.
- **Weak acids** are weak electrolytes that partially ionise only to a limited extent in water.
- **Strong bases** are strong electrolytes that ionise completely in water.
- **Weak bases** are weak electrolytes that ionise to a very limited extent in water.
- **Basicity** of an acid is the number of hydrogen ions that one molecule of an acid can produce.
- **Acidity** of a base is the number of molecules of a monoprotic acid that will neutralise one molecule of the base.
- **Acid dissociation constant (K_a)** is the equilibrium constant for a weak acid.
- **Base dissociation constant (K_b)** is the equilibrium constant for a weak base.

5.4 SALT HYDROLYSIS

When the solutions of an acid and a base are mixed, an acid-base neutralisation reaction occurs, forming salt and water. Salts are strong electrolytes that completely dissociate into ions in water. Water solutions of normal salts may be acidic, basic, or neutral depending on the salt. These differences are due to the reaction of ions of the salt and water. This reaction is referred to as hydrolysis. The term salt hydrolysis describes the reaction of an anion or a cation of a salt, or both, with water. **Salt hydrolysis** usually affects the pH of a solution. There are four possible cases as below.

(a) Salts of Strong Bases and Strong Acids

Consider a solution of NaCl, which is the salt of the strong base NaOH and the strong acid HCl. NaCl dissociates into Na^+ and Cl^- ions in H_2O. Water molecules ionise slightly to produce equal concentrations of H^+ and OH^- ions.

$$NaCl\,(s) \longrightarrow Na^+\,(aq) + Cl^-\,(aq)$$
$$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

The process may also be written as

$$H_2O\,(l) \rightleftharpoons \underset{OH^-\,(aq)}{Na^+\,(aq)} + \underset{H^+\,(aq)}{Cl^-\,(aq)}$$

The cation Na^+ and the anion Cl^- of the salt do not react with water. This is because the products, base and acid, are strong so that no formation of molecules, NaOH and HCl, occurs. Only Na^+, Cl^-, H^+ and OH^- ions are present in this salt solution. The ionic equilibrium

of water remains undisturbed. It means that there is no hydrolysis. Solutions of salts of strong bases and strong acids are therefore neutral (pH = 7) because neither ion of such a salt disturbs the equilibrium of water.

(b) Salts of Strong Bases and Weak Acids

Consider a solution of CH_3COONa, which is the salt of the strong base NaOH and the weak acid CH_3COOH. It is soluble and dissociates completely in water. Water molecules ionise slightly to produce equal concentrations of H^+ and OH^- ions.

$$CH_3COONa\ (aq) \longrightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$$
$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$

The cation Na^+ of the salt does not react with water. This is because the product base is so strong so that no formation of molecule, NaOH, occurs. It means that there is no hydrolysis. On the other hand, the anion CH_3COO^- of the salt is a strong conjugate base of the weak acid, CH_3COOH. Thus, it reacts to some extent with H^+ from H_2O to form CH_3COOH and OH^-.

$$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COOH\ (aq) + OH^-\ (aq)$$

This disturbs the equilibrium of water and more water molecules ionise to maintain K_w constant. This produces more OH^- ions and so the solution becomes basic (pH > 7).

(c) Salts of Weak Bases and Strong Acids

Consider a solution of NH_4Cl, which is the salt of the weak base NH_4OH and the strong acid HCl. It is soluble and dissociates completely in water. Water molecules ionise slightly to produce equal concentrations of H^+ and OH^- ions.

$$NH_4Cl\ (aq) \longrightarrow NH_4^+\ (aq) + Cl^-\ (aq)$$
$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$

The cation NH_4^+ of the salt is a strong conjugate acid of the weak base NH_4OH. Thus, it reacts to some extent with OH^- from H_2O to form NH_4OH and H^+. The anion Cl^- of the salt is a weak conjugate base of the strong acid HCl and it does not react with water.

$$NH_4^+\ (aq) + H_2O\ (l) \rightleftharpoons NH_4OH\ (aq) + H^+\ (aq)$$

This disturbs the equilibrium of water and more water molecules ionise to maintain K_w constant. This produces more H^+ ions and so, the solution becomes acidic (pH < 7).

(d) Salts of Weak Bases and Weak Acids

For a salt derived from a weak acid and a weak base, both the cation and the anion hydrolyse. However, whether a solution containing such a salt is acidic, basic, or neutral depends on the relative strengths of the weak acid and the weak base. Qualitative predictions about these solutions are based on the following:

(i) If K_b for the anion is greater than K_a for the cation ($K_b > K_a$), then the solution must be basic because the anion will react with water to a greater extent than the cation. At equilibrium, there will be more OH^- ions than H^+ ions (e.g., NH_4CN).

(ii) Conversely, if K_b for the anion is smaller than K_a for the cation ($K_b < K_a$), the solution will be acidic because the cation will react with water to a greater extent than the anion. At equilibrium, there will be more H^+ ions than OH^- ions (e.g., NH_4F).

(iii) If K_b for the anion is approximately equal to K_a for the cation ($K_b \approx K_a$), the solution will be nearly neutral because the anion produces OH^- ions just as the cation produces H^+ ions (e.g., CH_3COONH_4).

As an example, ammonium ethanoate, CH_3COONH_4, is the salt of the weak acid, CH_3COOH, and the weak base, NH_4OH. It is soluble and dissociates completely in water. Water molecules ionise slightly to produce equal concentrations of H^+ and OH^- ions.

$$CH_3COONH_4\,(aq) \longrightarrow NH_4^+\,(aq) + CH_3COO^-\,(aq)$$
$$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

The cation NH_4^+ of the salt is a strong conjugate acid of the weak base, NH_4OH. Thus, it reacts to some extent with OH^- from H_2O to form NH_4OH and H^+. The anion CH_3COO^- of the salt is a strong conjugate base of the weak acid, CH_3COOH. Thus, it reacts to some extent with H^+ from H_2O to form CH_3COOH and OH^-.

$$NH_4^+\,(aq) + H_2O\,(l) \rightleftharpoons NH_4OH\,(aq) + H^+\,(aq)$$
$$CH_3COO^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COOH\,(aq) + OH^-\,(aq)$$

K_b for the anion CH_3COO^- (5.6×10^{-10}) and K_a for the cation NH_4^+ (5.6×10^{-10}) are equal. Thus, the CH_3COO^- ions produce OH^- ions just as the NH_4^+ ions produce H^+ ions. Thus, ammonium ethanoate solution is neutral.

Example 9: Classify the following salts and predict whether the salt solutions will be acidic, basic, or nearly neutral: (i) $(NH_4)_2SO_4$ (ii) KNO_3 (iii) Na_2CO_3 and (iv) NH_4F
($K_a = 5.6 \times 10^{-10}$ for NH_4^+ and $K_b = 1.4 \times 10^{-11}$ for F^-)

Solution:
(i) $(NH_4)_2SO_4$ is the salt of the weak base, NH_4OH, and the strong acid, H_2SO_4. So, the salt solution is acidic.
(ii) KNO_3 is the salt of the strong base, KOH, and the strong acid, HNO_3. So, the solution is neutral.
(iii) Na_2CO_3 is the salt of the strong base, NaOH, and the weak acid, H_2CO_3. So, the solution is basic.
(iv) NH_4F is the salt of the weak base, NH_4OH, and the weak acid, HF. K_b for the anion, F^- (1.4×10^{-11}) is smaller than K_a for the cation, NH_4^+ (5.6×10^{-10}). Thus, the solution is acidic.

REVIEW QUESTIONS

(1) How can salts be classified into four classes? For each class, write the name and the formula of a salt that fits into that category.
(2) Write the balanced chemical equation for an acid-base reaction that would produce each of the following salts and predict whether an aqueous solution of each salt is acidic, basic, or neutral: (i) $CaCl_2$ (ii) HCOONa (iii) NH_4I
(3) What are the properties (acidic, basic or neutral) of the solutions obtained by dissolving the following salts in water?
(i) ammonium nitrate (ii) ammonium cyanide (iii) potassium chloride
($K_a = 5.6 \times 10^{-10}$ for NH_4^+ and $K_b = 2.5 \times 10^{-5}$ for CN^-)

Key Term

- **Salt hydrolysis** is the reaction of an anion or a cation of salt, or both, with water.

5.5 BUFFER SOLUTIONS

Buffers are very important to chemical and biological systems. The pH in the human body varies greatly from one fluid to another; for example, the pH of blood is about 7.4, whereas the gastric juice in a stomach has a pH of about 1.5. These pH values, which are crucial for proper enzyme function and the balance of osmotic pressure, are maintained by buffers in most cases. Many experiments, particularly in biochemistry, have to be performed in an aqueous solution. Although it is impossible to make a solution whose pH is unaffected, it is possible to make a solution whose pH is almost unchanged by adding a small amount of acid or base; such a solution is referred to as a buffer solution and a solute (salt) is known as a buffer.

A buffer solution is a solution that resists changes in pH as a result of dilution or small addition of acids or bases. The two common kinds of buffer solutions are solutions containing (1) a weak acid and its salt (conjugate base), and (2) a weak base and its salt (conjugate acid).

(a) Buffer Solution of a Weak Acid and Its Salt

A typical buffer solution for acidic values of pH (e.g., 4–7) contains a weak acid and its salt. A mixture of ethanoic acid and sodium ethanoate is commonly used.

Sodium ethanoate, a strong electrolyte, dissociates completely in water and provides a large reserve of ethanoate ions. Ethanoic acid provides a large potential reserve of H^+ ions.

$$CH_3COONa\,(aq) \longrightarrow Na^+\,(aq) + CH_3COO^-\,(aq)$$
$$CH_3COOH\,(aq) \rightleftharpoons H^+\,(aq) + CH_3COO^-\,(aq)$$

Function of a buffer of a weak acid and its salt

If a small amount of strong acid like HCl is added to this buffer solution, H^+ ions from the strong acid react with the base CH_3COO^- to form undissociated ethanoic acid. Therefore, the concentration of H^+ is reduced. This prevents a change in the pH of the solution.

$$H^+\,(aq) + CH_3COO^-\,(aq) \longrightarrow CH_3COOH\,(aq)$$

If a small amount of strong base like NaOH is added, the OH^- ions from the strong base react with undissociated ethanoic acid to form CH_3COO^- and undissociated water. Therefore, the concentration of OH^- is reduced. This prevents a change in the pH of the solution.

$$OH^-\,(aq) + CH_3COOH\,(aq) \longrightarrow CH_3COO^-\,(aq) + H_2O\,(l)$$

(b) Buffer Solution of a Weak Base and Its Salt

A buffer solution of pH 7–11 can be prepared with a weak base and its salt. A mixture of ammonium hydroxide (ammonia solution) and ammonium chloride is used.

Ammonium chloride, a strong electrolyte, dissociates completely in water and provides a large source of ammonium ions. Ammonium hydroxide provides a large potential source of OH^- ions.

$$NH_4Cl\,(aq) \longrightarrow NH_4^+\,(aq) + Cl^-\,(aq)$$
$$NH_4OH\,(aq) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

Function of a buffer of a weak base and its salt

If a small amount of strong base is added to this buffer solution, OH^- ions from the strong base react with the NH_4^+ ions to form NH_4OH. Therefore, the concentration of OH^- is reduced. This prevents a change in the pH of the solution.

$$OH^-(aq) + NH_4^+(aq) \longrightarrow NH_4OH(aq)$$

If a small amount of strong acid is added to this buffer solution, H^+ ions from the strong acid react with the NH_4OH to form NH_4^+ ions and undissociated water. Therefore, the concentration of H^+ ions is reduced. This prevents a change in the pH of the solution.

$$H^+(aq) + NH_4OH(aq) \longrightarrow NH_4^+(aq) + H_2O(l)$$

Example 10: Which of the following solutions are buffer solutions? Give reasons.
(i) HCN/NaCN (ii) HBr/KBr (iii) HCOOH/HCOOK (iv) $HClO_4/NaClO_4$

Solution:
(i) HCN/NaCN is a buffer solution because HCN is a weak acid and NaCN is its salt. CN^- is a conjugate base of HCN.
(ii) HBr/KBr is not a buffer solution because HBr is a strong acid.
(iii) HCOOH/HCOOK is a buffer solution because HCOOH is a weak acid and HCOOK is its salt. $HCOO^-$ is a conjugate base of HCOOH.
(iv) $HClO_4/NaClO_4$ is not a buffer solution because $HClO_4$ is a strong acid.

Example 11: Calculate the pH of a buffer solution containing 0.01 mol of ethanoic acid and 0.01 mol of sodium ethanoate per dm^3. ($K_a = 1.8 \times 10^{-5}$ for ethanoic acid)

Solution:

$$CH_3COONa(aq) \longrightarrow Na^+(aq) + CH_3COO^-(aq)$$
$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$
$$[CH_3COOH] = 0.01 \text{ mol dm}^{-3}$$
$$[CH_3COONa] = [CH_3COO^-] = 0.01 \text{ mol dm}^{-3}$$
$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$
$$1.8 \times 10^{-5} = \frac{[H^+] \times 0.01}{0.01}$$
$$[H^+] = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$
$$pH = -\log 1.8 \times 10^{-5} = -0.255 + 5 = 4.745$$

Example 12: The pH of a sodium ethanoate-ethanoic acid buffer is 4.50. Calculate the ratio of $[CH_3COO^-]$ and $[CH_3COOH]$. ($K_a = 1.8 \times 10^{-5}$ for ethanoic acid)

Solution:

$$CH_3COONa(aq) \longrightarrow Na^+(aq) + CH_3COO^-(aq)$$
$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$
$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$
$$pH = 4.50$$
$$-\log [H^+] = 4.50$$
$$[H^+] = \text{antilog} - 4.50$$
$$[H^+] = 3.16 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{K_a}{[H^+]} = \frac{1.8 \times 10^{-5}}{3.16 \times 10^{-5}} = 0.570$$

REVIEW QUESTIONS

(1) Which of the following solutions can be classified as buffer solutions? Explain your answer.
(i) H_2CO_3/HCO_3^- (ii) HCl/NaCl (iii) NH_3/NaOH (iv) HF/NaF

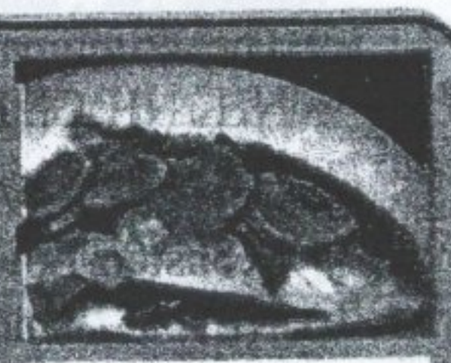
(2) A mixture of methanoic acid and sodium methanoate was made to be used as a buffer. If a small amount of dilute hydrochloric acid is added to this solution, the pH does not change much. Explain what would happen to the extra hydrogen ions added.

(3) A buffer solution is prepared by dissolving 0.2 g of HF and 0.42 g of NaF in 0.2 dm^3 of water. Calculate the pH of this buffer solution. (pK_a of HF = 3.14; Na = 23, H = 1, F =19)

Key Term

- **Buffer solution** is a solution that resists changes in pH as a result of dilution or a small addition of acids or bases.

Chemistry in Society



- The odour of fish is due to the presence of amines (weak bases). By using lemon juice or vinegar on cooked fish, a neutralisation reaction takes place between citric acid (weak acid) in lemons or ethanoic acid (weak acid) in vinegar and the bases in the flesh of fish. Thus, it reduces the odour of the fish.
- When there is too much acid (HCl) in the stomach, this acid can cause a lot of pain. Antacids such as aluminium hydroxide, magnesium hydroxide (milk of magnesia), and sodium hydrogen carbonate which are bases, are taken to neutralise the acids so that they do not burn as much.
- The body lotion is buffered to a slightly acidic pH to relieve rashes. This inhibits the growth of bacteria and other pathogens.
- Vitamin C (ascorbic acid), especially in higher doses, can cause significant stomach upset. Buffered vitamin C contains ascorbic acid together with calcium, magnesium, and potassium ascorbates to allow higher doses without causing stomach upset.
- Bacteria present in the human mouth eat the adhering part of the food in it and produce acid. Tooth decay is the result of this acid attacking the calcium compound that makes up the tooth's enamel. The acid inside the mouth is neutralised by toothpaste, preventing tooth decay.

EXERCISES

Q 1 to Q 6 (Remembering and Understanding)

1. Fill in the blanks with a suitable word or phrase or numerical value with the unit as necessary.
   (a) The stronger an acid, the _____ is its conjugate base.
   (b) A solution with pOH of 3.0 would be described as a(an)_____ solution.
   (c) The symbol for the dissociation constant of a weak base is _____.
   (d) The concentration of OH^- is _____ for a 0.1 mol dm^{-3} strong $Ba(OH)_2$ solution.
   (e) A buffer solution resists the change of _____.
2. Select the correct word or words given in the brackets.
   (a) In pure water, the statement of ($[H^+] = 1.0 \times 10^{-7}$ mol dm^{-3}, pH = 7.0, $[H^+] = [OH^-]$) is always correct at all conditions of temperature and pressure.
   (b) Lewis bases are defined as (proton donors, electron donors, proton acceptors).
   (c) Increasing order of pH of the given solutions is -
   (ammonia < ethanoic acid < sodium hydroxide < nitric acid,
   nitric acid< ethanoic acid < ammonia < sodium hydroxide,
   nitric acid < ethanoic acid < sodium hydroxide < ammonia).
   (d) When NaCN dissolves in water, the pH becomes greater than 7 because of the hydrolysis of (cation Na^+, anion CN^-, both cation Na^+ and anion CN^-).
   (e) The combination that would buffer the pH at about 9 is (CH_3COOH/CH_3COONa, NH_3/NH_4Cl, HCl/NaCl).
3. (a) Describe how Lewis define an acid and a base. In what way are they more general than the Brønsted-Lowry definitions?
   (b) Write a balanced chemical equation for the dissociation of each of the following Brønsted-Lowry acids in water. What is the conjugate base of each acid?
   (i) HSO_4^- (ii) NH_4^+ (iii) H_3O^+
4. (a) Describe the acid-base properties of water in the Brønsted-Lowry framework.
   (b) What is the conjugate acid of each of the following Brønsted-Lowry bases ?
   (i) HCO_3^- (ii) CO_3^{2-} (iii) OH^-

Q 5 to Q 14 (Analysing and Problem solving)

5. For each of the following equations, indicate whether the substance (bold-typed) is acting as a Brønsted–Lowry acid or a Brønsted–Lowry base. State which species is its conjugate base or conjugate acid.
   (i) $Br^-(aq) + \mathbf{HSO_4^-}(aq) \rightleftharpoons HBr(aq) + SO_4^{2-}(aq)$
   (ii) $NH_3(l) + \mathbf{H_2O}(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
   (iii) $\mathbf{HS^-}(aq) + HF(aq) \rightleftharpoons F^-(aq) + H_2S(aq)$
6. Give an example of (i) a weak acid that has oxygen atoms (ii) a weak acid that has no oxygen atoms (iii) a neutral molecule that acts as a Lewis acid (iv) a neutral molecule that acts as a Lewis base (v) a weak acid that has two ionisable H atoms (vi) a conjugate acid-base pair both of which react with HCl to give carbon dioxide gas.

7. (a) Calculate the pH of each of the following solutions:
   (i) A sample of seawater that has a hydroxide ion concentration of 1.58×10^{-6} mol dm^{-3}
   (ii) A sample of black coffee that has a hydrogen ion concentration of 7.8×10^{-6} mol dm^{-3}
   (iii) A fruit juice containing a monoprotic acid HA that has a hydrogen ion concentration of 2.5×10^{-4} mol dm^{-3}
   (b) Calculate the hydrogen ion concentration of solutions having pH values of -
   (i) 8.3 (ii) 3.6 (iii) 12.4.

8. Calculate K_a and pK_a of a 0.1 mol dm^{-3} solution of lactic acid (a weak monoprotic acid, HX) whose pH is 2.4.

9. The pOH of a strong base solution is 1.88 at 25 °C. Calculate the concentration of the base (i) if the base is KOH (ii) if the base is $Ba(OH)_2$.

10. Write a chemical equation that represents the equilibrium between water and a weak base, B.
   (i) Write the equilibrium constant expression for this reaction.
   (ii) What is the symbol used for this equilibrium constant?
   (iii) Calculate the pH of a 0.24 mol dm^{-3} solution of a weak base with a K_b of 3.5×10^{-6}.

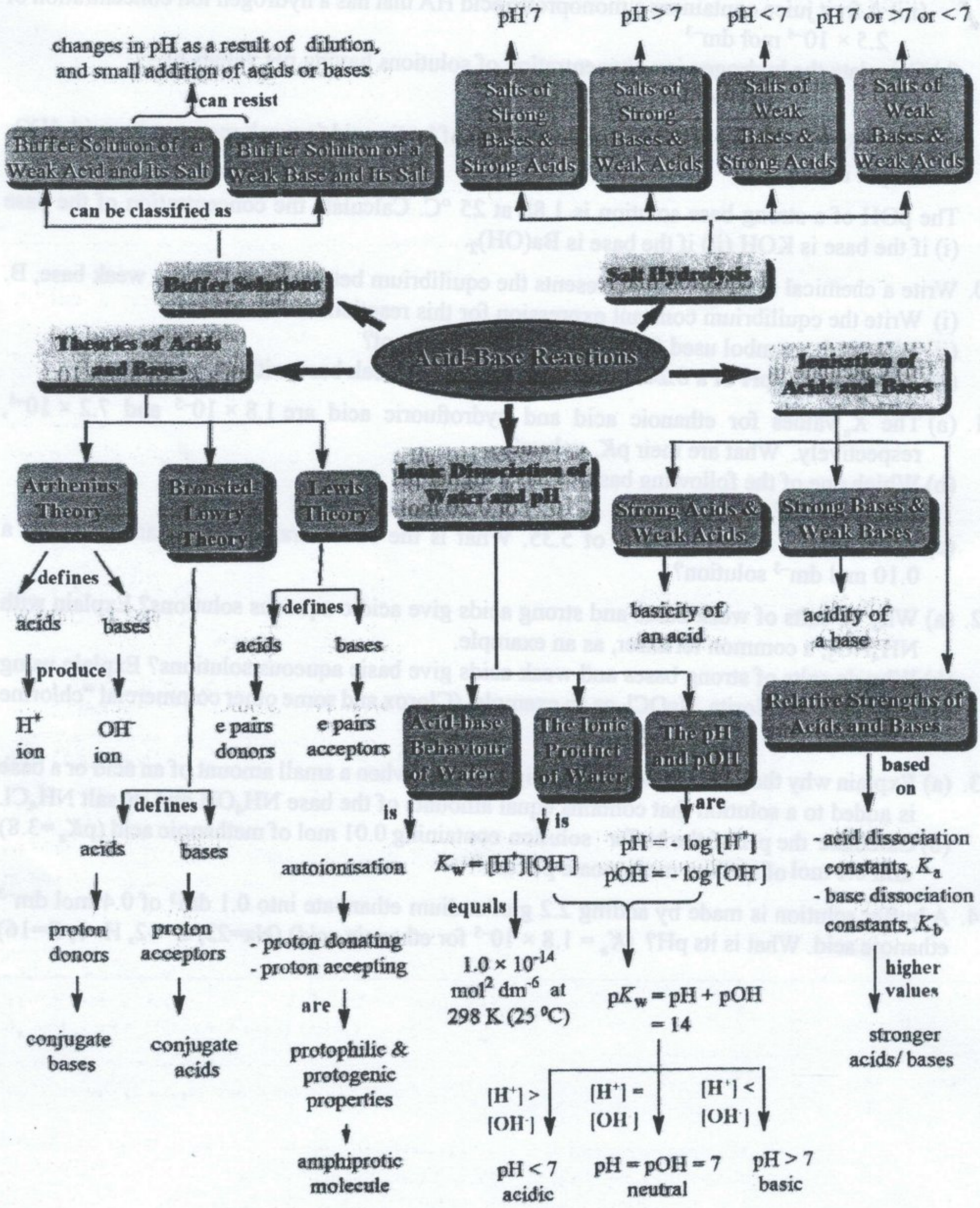
11. (a) The K_a values for ethanoic acid and hydrofluoric acid are 1.8×10^{-5} and 7.2×10^{-4}, respectively. What are their pK_a values?
   (b) Which one of the following bases has a higher pH?
   0.20 mol dm^{-3} NH_3 ($K_b = 1.8 \times 10^{-5}$) or 0.20 mol dm^{-3} NaOH
   (c) A weak acid, HA, has a pK_a of 5.35. What is the concentration of the anion, A^-, in a 0.10 mol dm^{-3} solution?

12. (a) Why do salts of weak bases and strong acids give acidic aqueous solutions? Explain with NH_4NO_3, a common fertiliser, as an example.
   (b) Why do salts of strong bases and weak acids give basic aqueous solutions? Explain using sodium hypochlorite, NaOCl, as an example. (Clorox and some other commercial "chlorine bleaches" are 6 % NaOCl.)

13. (a) Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_4OH and its salt NH_4Cl.
   (b) Calculate the pH of the buffer solution containing 0.01 mol of methanoic acid ($pK_a = 3.8$) and 0.1 mol of sodium methanoate per dm^3.

14. A buffer solution is made by adding 2.2 g of sodium ethanoate into 0.1 dm^3 of 0.4 mol dm^{-3} ethanoic acid. What is its pH? ($K_a = 1.8 \times 10^{-5}$ for ethanoic acid) (Na=23, C=12, H=1, O=16)

CHAPTER REVIEW
(Concept Map)



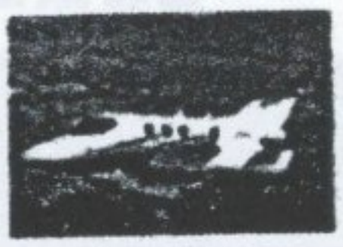
CHAPTER 6

TRANSITION ELEMENTS

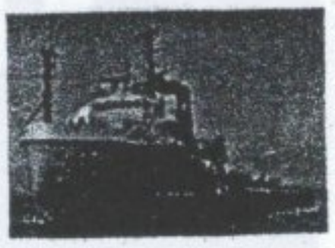
Transition elements are the metals that exist in the block between Groups II and III that is, they are in Groups 3 to 12 of the Periodic Table. Transition elements such as iron and copper have played an important role in our lives. Iron is still important as a structural material and used as a catalyst in the manufacture of ammonia. It is also present in haemoglobin. Copper is important as an electronic conductor. Copper-nickel (cupronickel) alloys are used in shipbuilding due to their excellent resistance to seawater corrosion. Gold is the transition element that is used as jewellery because of its beautiful yellow lustre colour and its inertness to oxygen and water. Other transition elements are also useful. For example, titanium is a major component in modern jet aircraft and is used in manufacturing artificial joints and dental implants. The role of cobalt, an essential component of vitamin B_{12} in living systems, is equally important. A very tiny trace amount of chromium is detected in apples. Because of their distinctive properties and uses as catalysts, structural materials, and jewellery in our daily lives, it is very important to study the chemistry of the transition elements. In this chapter, the general properties and characteristics, and uses of the *d*-block transition elements, especially the first row transition elements between the *s*-block element calcium and the *p*-block element gallium are discussed.

Iron bridge

Gold jewellery



Titanium jet aircraft



Cupronickel alloy used in shipbuilding

Learning Outcomes

After completing this chapter, students will be able to:

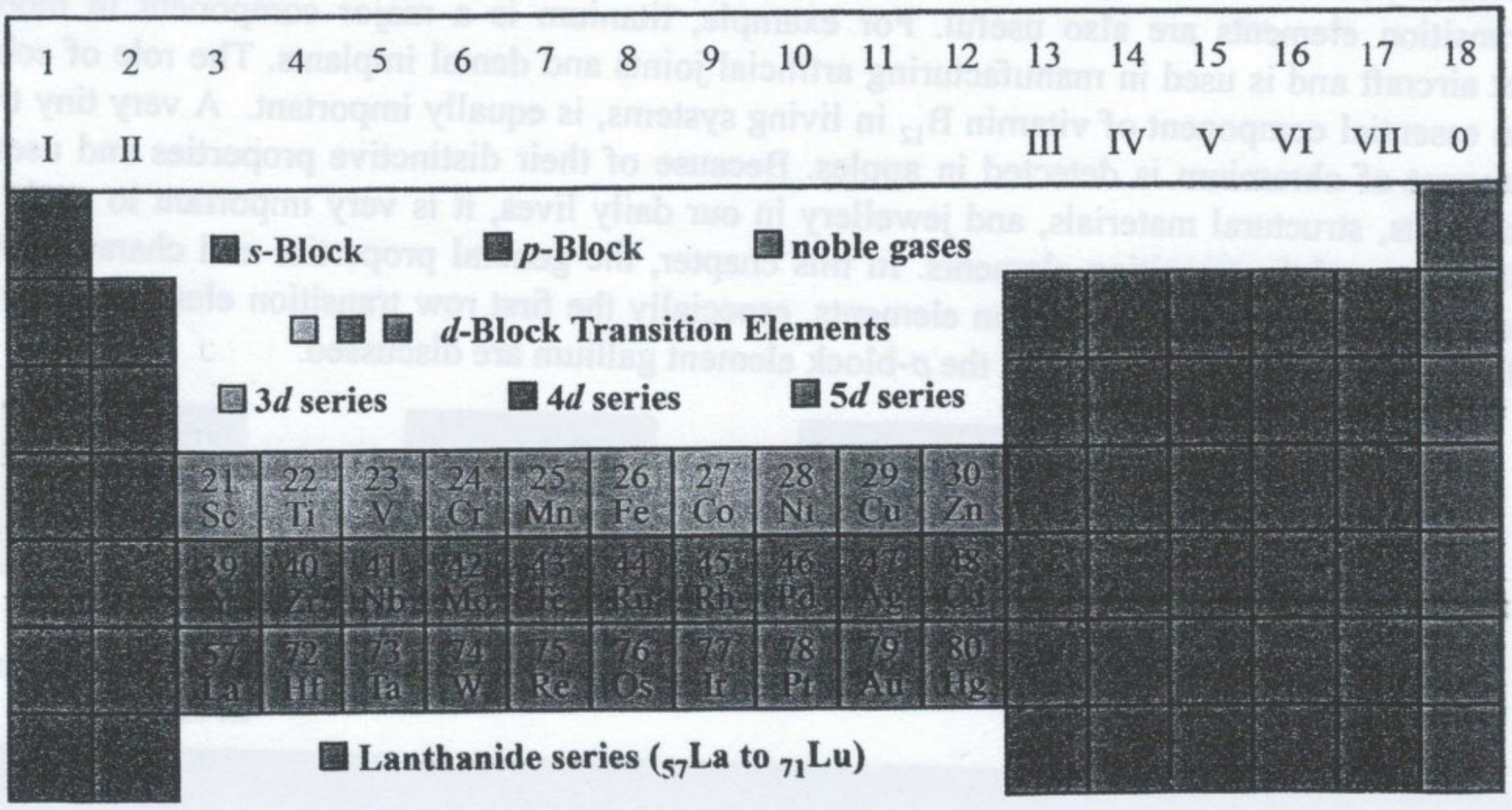
- indicate the position of the *d*-block transition elements in the Periodic Table;
- describe the electronic configuration of the first series (3*d* series) of transition elements and their ions;
- explain the general properties and the characteristics of the first series of transition elements, focusing on their variable oxidation states, formation of coloured compounds and ions, and magnetic and catalytic properties;
- describe the use of transition elements in different areas of daily life.

6.1 THE 3*d* SERIES TRANSITION ELEMENTS

The transition elements are located between Group II of the *s*-block and Group III of the *p*-block elements in the Periodic Table. IUPAC defines a transition element (metal) as an element whose atom has partially filled *d* subshells (orbitals) or which can give rise to cations with incomplete *d* subshells (orbitals).

Under this definition, groups 3 to 12 are the transition elements and the *f*-block lanthanide and actinide series are called the inner transition elements.

There are mainly three series of transition elements. The first series 3*d* transition elements run from scandium ($_{21}$Sc) through zinc ($_{30}$Zn). The second series 4*d* transition elements run from yttrium ($_{39}$Y) through cadmium ($_{48}$Cd), and the third series 5*d* transition elements run from lanthanum ($_{57}$La) through mercury ($_{80}$Hg) except 14 elements of lanthanide series from cerium ($_{58}$Ce) to lutetium ($_{71}$Lu). The transition elements are also called the *d*-block elements because the *d* orbitals are filled in these elements. (The transition elements Zn, Cd, and Hg are sometimes called transition metals, but they do not have this characteristic electronic configuration as defined by the IUPAC, so they really do not belong in this category.) In this section, the 3*d* series transition elements, from scandium to zinc, will be highlighted.



(a) The First Series 3*d* Transition Elements

The first row of the transition elements is in the fourth row (Period 4) of the Periodic Table. In the 3*d* series, there are 10 transition elements, namely, scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn).

For the 3*d* series transition elements, the nuclear charge increases from scandium to copper so that atomic radii show a gradual decrease in their values (Table 6.1). The decrease in atomic radii occurs because the attraction force between the nucleus and electrons is stronger than the electron-electron repulsion force. Compare to *s*- and *p*-block elements, the decrease is less rapid. All the transition elements in this series have quite similar radii, which accounts for their ability to blend together to form alloys. Similarly, the first ionisation energies (IE) of scandium to copper increase only slightly as the positive charge on the nucleus (atomic number) increases. The trend correlates with an increase in the nuclear charge and a decrease in the atomic radius. However, towards the end of the series, zinc has the larger atomic size and ionisation energy due to the increasing electron-electron repulsion as the occupancy of the *d* orbitals is completed.

Table 6.1 Periodic Properties of the 3*d* Series Transition Elements

Properties	Periodic properties of elements Sc to Zn									
	$_{21}$Sc	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{25}$Mn	$_{26}$Fe	$_{27}$Co	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn
Atomic radius (pm)	162	147	134	130	135	126	125	124	128	138
First IE (kJ mol^{-1})	631	658	650	652	717	759	760	736	745	906

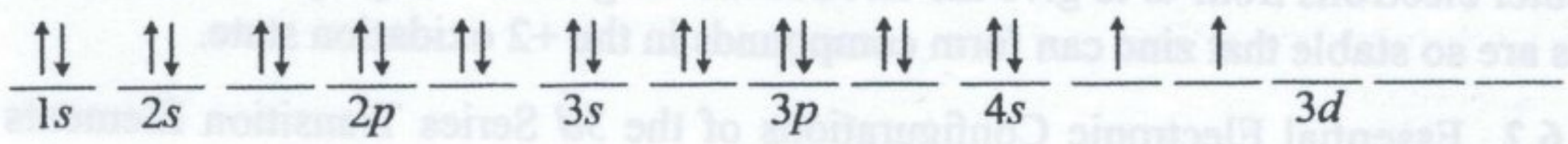
(b) Electronic Configurations of the 3*d* Series Transition Elements

(i) Electronic configurations of atoms

Although the 4*s* orbital is the outermost orbital, it is slightly lower in energy than the 3*d* orbitals. In atoms of the transition elements, the 4*s* orbital is normally filled and the rest of the electrons occupy the 3*d* orbitals. The electronic configurations of the 3*d* series transition elements will be discussed in this section.

The filling of the 3*d* orbitals generally starts from scandium ($_{21}$Sc) and continues up to zinc ($_{30}$Zn), in which the orbital is completely filled. The filling of the 3*d* orbitals generally obeys Hund's rule, with one electron added to each of the five *d* orbitals before a second electron is added to any one of them. For example, the complete electronic configuration of titanium ($_{22}$Ti) can be described below.

$_{22}$Ti: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$



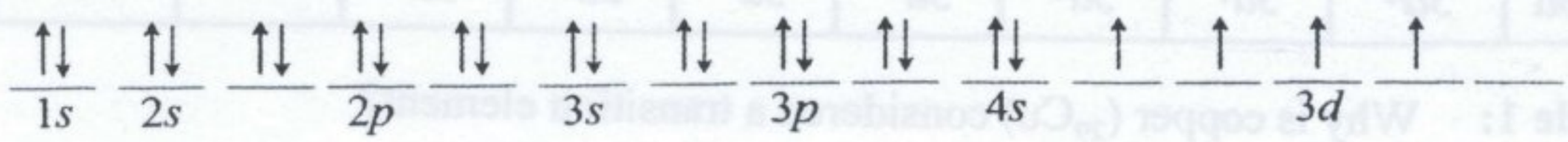
Since the electronic configuration of $_{18}$Ar is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$, it can be represented an argon core as [Ar].

Thus, $_{22}$Ti can also be represented using the argon core as [Ar] $4s^2\ 3d^2$ and its essential electronic configuration is represented as $4s^2\ 3d^2$.

There are two exceptions to the expected regular filling pattern (half-filled or completely filled orbitals); chromium ($_{24}$Cr) and copper ($_{29}$Cu).

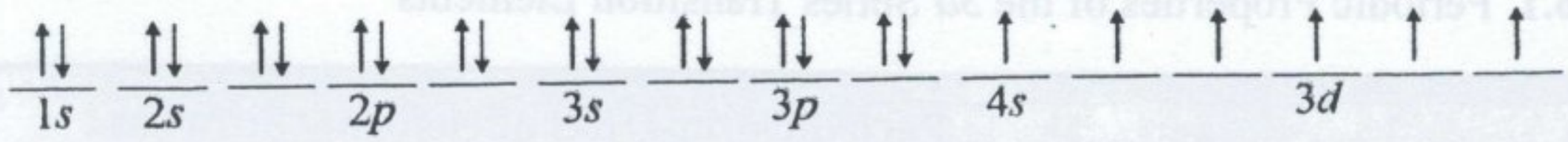
In the case of $_{24}$Cr, the expected complete electronic configuration is shown below.

$_{24}$Cr: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4$



However, 3*d* and 4*s* orbitals have nearly the same energy. So, each of these orbitals must be filled with each electron to attain a more stable electronic configuration with the half-filled 3*d* orbitals. So, one electron from the 4*s* shifts to the 3*d* orbitals.

$_{24}Cr$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

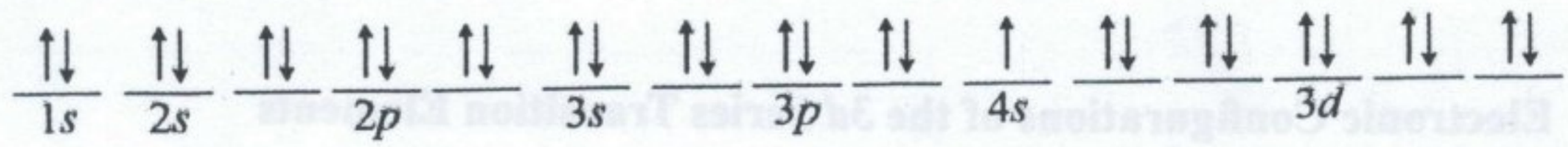


[Ar] $4s^1\ 3d^5$

Essential electronic configuration of $_{24}Cr$: $4s^1\ 3d^5$

Similarly, the electronic configuration of $_{29}Cu$ is [Ar] $4s^1\ 3d^{10}$, instead of the expected [Ar] $4s^2\ 3d^9$. This is so because completely filled $3d$ orbitals have extra stability.

$_{29}Cu$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$



In general, the neutral atoms of most of the transition elements have an essential electronic configuration of **(n-1)$d^{1\text{-}10}$ n$s^{1\text{-}2}$**.

(ii) Electronic configurations of the ions

In the transition metal elements, the $4s$ orbital is the outermost orbital. When these metals form ions, the electrons are always removed first from the $4s$ orbital and then from the $3d$ orbitals. The electronic configuration of the iron(II) ion (Fe^{2+}) is [Ar] $3d^6$, and the electronic configuration of the iron(III) ion (Fe^{3+}) is [Ar] $3d^5$.

In general, the ions of transition elements have an electronic configuration of **(n-1)$d^{1\text{-}10}$**. The essential electronic configurations of the $3d$ series transition elements and their ions are shown in Table 6.2.

The zinc element has completely filled $3d$ orbitals. When it forms an ion, it always loses the 2 outer electrons from $4s$ to give the electronic configuration of [Ar] $3d^{10}$. Completely filled $3d$ orbitals are so stable that zinc can form compounds in the +2 oxidation state.

Table 6.2 Essential Electronic Configurations of the $3d$ Series Transition Elements and Their Ions (M^{2+} and M^{3+} Ions)

Element	Essential electronic configuration									
	$_{21}Sc$	$_{22}Ti$	$_{23}V$	$_{24}Cr$	$_{25}Mn$	$_{26}Fe$	$_{27}Co$	$_{28}Ni$	$_{29}Cu$	$_{30}Zn$
M atom	$3d^1\ 4s^2$	$3d^2\ 4s^2$	$3d^3\ 4s^2$	$3d^5\ 4s^1$	$3d^5\ 4s^2$	$3d^6\ 4s^2$	$3d^7\ 4s^2$	$3d^8\ 4s^2$	$3d^{10}\ 4s^1$	$3d^{10}\ 4s^2$
M^{2+} ion	-	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
M^{3+} ion	$3d^0$	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	-

Example 1: Why is copper ($_{29}Cu$) considered a transition element?

Solution: $_{29}Cu$ has the electronic configuration, [Ar] $3d^{10}\ 4s^1$.
Cu^{2+} ion has the electronic configuration, [Ar] $3d^9$.
Copper is considered a transition element because the Cu^{2+} ion has incomplete $3d$ orbitals.

REVIEW QUESTIONS

(1) Choose the transition elements from the following:
$_{11}Na$, $_{24}Cr$, $_{3}Li$, $_{12}Mg$, $_{22}Ti$, $_{20}Ca$, $_{13}Al$, $_{26}Fe$, $_{28}Ni$, $_{25}Mn$
Write the complete electronic configurations for the transition elements of choice.

(2) Write down the essential electronic configurations of the metals and ions listed below.
(i) Sc (ii) Fe^{2+} (iii) Co (iv) Cu (v) Zn^{2+}
Given: $_{21}Sc$, $_{26}Fe$, $_{27}Co$, $_{29}Cu$, $_{30}Zn$

(3) (a) Using an argon core, give the complete electronic configurations of the following species:
(i) V^{2+} (ii) Cr^{3+} (iii) Mn^{2+} (iv) Co^{3+} (v) Ni^{2+}
Given: $_{23}V$, $_{24}Cr$, $_{25}Mn$, $_{27}Co$, $_{28}Ni$

(b) State the number of 3*d* electrons in the following:
(i) Fe (ii) Fe^{3+} (iii) Mn (iv) Mn^{3+} (v) Co (vi) Co^{3+}
Given: $_{25}Mn$, $_{26}Fe$, $_{27}Co$

Key Term

- **Transition elements** are elements that have partially filled *d* subshells (orbitals) which can give rise to cations with incomplete *d* subshells (orbitals).

6.2 CHARACTERISTIC PROPERTIES OF THE 3*d* SERIES TRANSITION ELEMENTS

In a period, the properties of transition elements are very similar in contrast to those of *s*-block and *p*-block elements. This is because, in a transition series, the valence shell electronic configuration of the elements does not change. However, they have the same group similarities as the *s*-block and *p*-block elements. Most of the first series of transition elements are more familiar and technically important than the heavier members of their groups.

(a) General Properties of the 3*d* Series Transition Elements

Many of the properties of transition elements are similar, but they are very different from other metals in Groups I and II (alkali and alkaline earth metals). The general physical and chemical properties of 3*d* series transition elements are given below.

Physical properties

These transition elements are solid metals. They have typical metallic properties such as malleability, ductility, metallic lustre, and high tensile strength. They are silvery-white except for copper, which is brownish-red in colour. They are generally good conductors of electricity and heat. They have high melting points and boiling points as shown in Table 6.3. The transition elements have a high density. One cubic centimetre (1 cm^3) cube of iron is 8 times heavier than a 1 cm^3 cube of sodium.

Table 6.3 Physical Properties of the 3*d* Series Transition Elements

Properties	$_{21}$Sc	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{25}$Mn	$_{26}$Fe	$_{27}$Co	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn
Melting point (°C)	1539	1668	1900	1875	1245	1536	1495	1453	1083	420
Boiling point (°C)	2730	3260	3450	2665	2150	3000	2900	2730	2595	906
Density (g cm^{-3})	3.0	4.5	6.1	7.2	7.4	7.9	8.9	8.9	9.0	7.1

Chemical properties

Transition elements have a wide range of chemical behaviours.

They are significantly less reactive than Group I metals. For example, nickel and copper do not react with water, or catch fire in the air (oxygen), unlike sodium. In general, transition metals do not corrode readily in the atmosphere. But iron is an exception; it rusts easily. They readily form alloys. Iron combined with non-metal carbon produces an alloy called steel.

Iron(III) oxide (reddish-brown)

Iron(II) sulphate (green)

Copper(II) sulphate (blue)

Most transition elements form coloured compounds. In contrast, the Groups I and II metals form white compounds. Most of them can form ions with different charges. So, the transition elements show variable oxidation states, and they can form more than one compound with another element, e.g., copper(I) oxide (Cu_2O), copper(II) oxide (CuO), iron(II) oxide (FeO), and iron(III) oxide (Fe_2O_3). Most transition elements can form **complex ions**.

Comparison of some properties of 3d series transition metals with the Group I alkali metals

The comparison of some properties of 3*d* series transition metals with the Group I alkali metals is summarised in Table 6.4.

Table 6.4 Comparison of Some Properties of the 3*d* Series Transition Metals and the Alkali Metals

Property	3*d* series Transition metals	Alkali metals
melting point	high	low
density	high	low
strength	strong and hard	soft
compounds	coloured	white or colourless
oxidation states	variable (e.g., Cu^+, Cu^{2+})	always + 1 (e.g., Na^+)
reactivity	low (do not react vigorously with water or oxygen)	high (react vigorously with water or oxygen)

(b) Characteristics of the 3*d* Series Transition Elements

Transition elements typically have incompletely filled *d* orbitals or readily give rise to ions with partially filled *d* orbitals. This is responsible for several notable properties, including variable oxidation states, distinctive colour, the formation of paramagnetic compounds, and catalytic activity.

Table 6.3 Physical Properties of the 3*d* Series Transition Elements

Properties	$_{21}$Sc	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{25}$Mn	$_{26}$Fe	$_{27}$Co	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn
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Iron(III) oxide (reddish-brown)

Iron(II) sulphate (green)

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Comparison of some properties of 3d series transition metals with the Group I alkali metals

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Property	3*d* series Transition metals	Alkali metals
melting point	high	low
density	high	low
strength	strong and hard	soft
compounds	coloured	white or colourless
oxidation states	variable (e.g., Cu^+, Cu^{2+})	always + 1 (e.g., Na^+)
reactivity	low (do not react vigorously with water or oxygen)	high (react vigorously with water or oxygen)

(b) Characteristics of the 3*d* Series Transition Elements

Transition elements typically have incompletely filled *d* orbitals or readily give rise to ions with partially filled *d* orbitals. This is responsible for several notable properties, including variable oxidation states, distinctive colour, the formation of paramagnetic compounds, and catalytic activity.

Variable oxidation states

Transition elements exhibit variable oxidation states. These elements usually lose the electron from the *s* orbital first, which is followed by the removal of an electron from the *d* orbitals. Because of the removal of electrons from *d* orbitals, transition elements show multiple oxidation states. Table 6.5 shows the oxidation states of the 3*d* series transition elements from scandium ($_{21}$Sc) to zinc ($_{30}$Zn). The +3 oxidation states (i.e., M^{3+} ions) are more stable at the beginning of the series, i.e., the left side of Mn whereas towards the end, i.e., the right side of Mn, +2 oxidation states (i.e., M^{2+} ions) are more stable.

The elements in the middle of the series exhibit more oxidation states than those to the left or right. Iron ($_{26}$Fe) is known to form oxidation states from +2 to +6, with iron(II) and iron(III) being the most common. The highest oxidation state is +7 for manganese ($_{25}$Mn). The ions of chromium, manganese, and iron have the highest oxidation states, +6, +7, and +6, respectively. These ions tend to be good oxidising agents, e.g., dichromate ion ($Cr_2O_7^{2-}$), permanganate ion (MnO_4^-), and ferrate(VI) ion (FeO_4^{2-}). In contrast, vanadium and chromium ions with the lowest oxidation state of +2 are good reducing agents, such as vanadium(II) ion (V^{2+}) and chromium(II) ion (Cr^{2+}). Because of their greater nuclear attraction force, divalent ions of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} are poor reducing agents. Transition metals usually have their highest oxidation states in compounds with high electronegative elements such as oxygen and fluorine. Examples are vanadium(V) fluoride (VF_5), chromium(VI) oxide (CrO_3), and manganese(VII) oxide (Mn_2O_7).

Table 6.5 Oxidation States of the 3*d* Series Transition Elements

Oxidations states of the transition elements									
$_{21}$Sc	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{25}$Mn	$_{26}$Fe	$_{27}$Co	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn
				+7					
			+6	+6	+6				
		+5	+5	+5	+5				
	+4	+4	+4	+4	+4	+4			
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
								+1	

Note: The stable oxidation states are shown in red colour.

Formation of coloured compounds and ions

The transition elements usually form coloured compounds and ions. The colour of compounds of transition metals is due to the presence of incomplete *d* orbitals or the presence of unpaired electrons. The transition metal compounds form coloured ions in an aqueous solution because they absorb part of the visible light and transmit the complement colour. The colour of some transition metal ions in an aqueous solution is given in Table 6.6. The characteristic colour of transition metal ions is helpful when performing qualitative analysis.

Table 6.6 The Colour of the 3*d* Series Transition Metal Ions in Aqueous Solutions

Ion	Colour	Ion	Colour	Ion	Colour
Ti^{3+}	purple	Cr^{3+}	violet	Fe^{2+}	green
V^{5+}	yellow	Cr^{2+}	blue	Co^{3+}	blue
V^{4+}	blue	Mn^{7+}	purple	Co^{2+}	pink
V^{3+}	green	Mn^{3+}	purple-red	Ni^{2+}	green
V^{2+}	violet	Mn^{2+}	pale pink	Cu^{2+}	blue
Cr^{6+}	yellow	Fe^{3+}	yellow		

Note: Sc^{3+} and Zn^{2+} ions are colourless because Sc^{3+} ion has completely empty *d* orbitals, and Zn^{2+} has completely filled *d* orbitals.

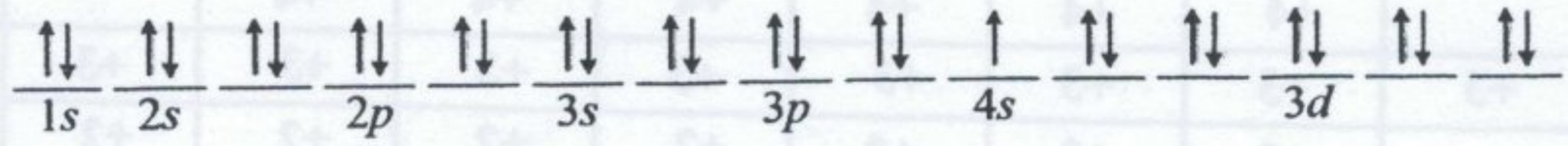
Magnetic property

The magnetic properties of a transition metal can be determined by examining the paired or unpaired electrons in (n-1)*d* orbitals. If the electrons are unpaired then it is a **paramagnetic substance**. If the electrons are paired, then it is a **diamagnetic substance**. According to the electronic configurations of the 3*d* series transition elements, scandium, titanium, vanadium, chromium, and manganese are paramagnetic substances whereas copper and zinc are diamagnetic substances. Most of the transition elements and their compounds are paramagnetic.

Substances that are attracted very strongly by the applied magnetic field are said to be ferromagnetic. Iron, cobalt, and nickel are **ferromagnetic substances**.

Example 2: Is copper ($_{29}Cu$) considered a diamagnetic substance? Give a reason for your answer.

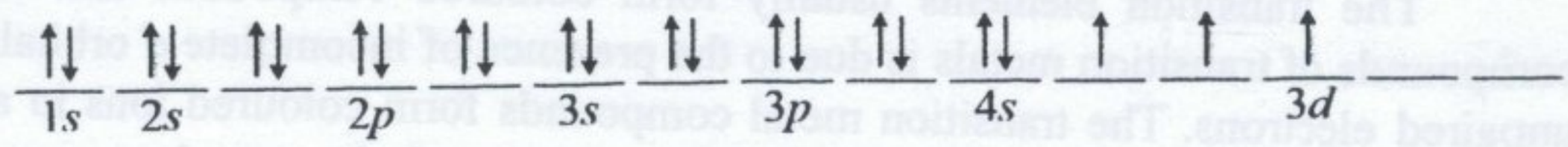
Solution: $_{29}Cu$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$



The electronic configuration of copper ($_{29}Cu$) is [Ar] $3d^{10}\ 4s^1$ which has the paired electrons in *d* orbitals. Therefore, it is a diamagnetic substance

Example 3: Is vanadium ($_{23}V$) considered a paramagnetic substance? Give a reason for your answer.

Solution: $_{23}V$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$



The electronic configuration of vanadium ($_{23}V$) is [Ar]$3d^3 4s^2$ which has unpaired electrons in the *d* orbitals. Therefore, it is a paramagnetic substance.

Catalytic property

Transition metals are widely used at the industrial level due to their catalytic properties. Many transition elements and their compounds act as good catalysts for specific reactions. Iron and vanadium are the most important catalysts. Iron is used as a catalyst in the manufacture of ammonia (Haber process). Vanadium is used in the form of vanadium(V) oxide (V_2O_5) in the manufacture of sulphuric acid (Contact process). Nickel is used as a catalyst in the hydrogenation of alkenes. Titanium(IV) chloride ($TiCl_4$) is used for the manufacturing of high-density polyethene in industries.

REVIEW QUESTIONS

(1) (a) List three properties of transition metals that are different from the metals in Group I.
(b) Select the correct property for the transition elements.
(i) soft or hard (ii) high density or low density
(iii) high melting point or low melting point (iv) reactive or unreactive with water

(2) (a) What are the characteristic properties of transition elements? Give any three.
(b) Write oxidation states for the following elements:
chromium, manganese, iron, nickel, and copper

(3) (a) What is the colour of each of the following ions?
(i) Ti^{3+} (ii) Cr^{3+} (iii) Mn^{2+} (iv) Fe^{2+} (v) Zn^{2+}
(b) Copper ($_{29}Cu$) and zinc ($_{30}Zn$) are diamagnetic; why?
(c) Name the transition metal catalysts used for each of the following manufacturing processes:
(i) Haber process (ii) Contact process

Key Terms

- **Complex ion** is an ion, which has a metal ion at its centre with a number of other molecules or ions surrounding it.
- **Paramagnetic substance** is a substance that has unpaired electrons and shows weak attraction towards the external magnetic field.
- **Diamagnetic substance** is a substance that has no unpaired electrons and shows no attraction (slight repulsion) from the external magnetic field.
- **Ferromagnetic substance** is a substance that is strongly attracted by the applied magnetic field, and retains its magnetisation for some time even after the external magnetic field is removed.

6.3 USES OF THE 3*d* SERIES TRANSITION ELEMENTS

Transition metals and their compounds have great importance in our lives. They are often known as everyday metals. Almost all of them are good at conducting both heat and electricity, making them useful for a variety of applications. The 3*d* series transition metals such as titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper have a wide range of uses. In this section, some of the various applications of 3*d* series transition metals and their compounds will be highlighted.

Applications in building materials

The transition elements such as iron, chromium, titanium etc., are used in building materials due to their properties of strength, malleability, and ductility. The uses of some elements are described below.

Titanium is an integral part of modern construction because it is highly corrosion-resistant, strong, and lightweight. It is used for roofs, flooring, and ceiling decoration in buildings. It is also used for spacecraft, ships, and marine equipment.

Iron is usually too soft to be used as metal alone. It is usually mixed with small amounts of other elements to make harder alloy steels with greater tensile strength and stronger than iron, but easily shaped. Iron alloy steels are strong, easily shaped, and cheap compared to most other metals. So, it is used for making building materials in construction, for example, bridges, buildings, ships, and cars.

Manganese is mainly used in alloys, such as steel. Steel contains about 1 % manganese to increase the strength and also improve workability and resistance. Manganese steel is extremely strong and is used for railway tracks.

Applications in industry

Transition metals and their compounds have many chemical and physical properties that make them desirable for industrial applications. They have a wide range of uses. Their properties are very similar but not identical. It is important to choose the suitable transition metal for the required purpose.

Vanadium is used to form alloys of steel with iron. In the chemical industry, vanadium metal sheets, wires and tubes are widely used. Vanadium can be used in the ceramics industry. Vanadium compounds are also used in several applications such as vanadium(V) oxide (V_2O_5) as a catalyst in the ceramics industry, and as a mordant in the printing and dyeing of fabrics.

Chromium has many industrial uses due to its toughness and resistance to heat and corrosion. It is widely used for manufacturing stainless steel. Various chromium salts are the main raw materials in the chemical industry. Chromium is mainly used in electroplating, tanning, printing, dyeing, catalysts, oxidants, matches, and metal corrosion inhibitors. In the automobile industry, chromium is involved in the production of car brake pads.

Manganese is used as a catalyst to reduce the octane rating in gasoline. It is also used in dry cell batteries, and paint.

Cobalt is used in making alloys with various metals. Cobalt ion has brilliant blue colour used as paint, ink, and pigments. It is primarily used in the ceramics and paint industry to create the blue colour. Rechargeable batteries are made up of cobalt.

Nickel is used for anti-corrosion coating, and nickel plating. It is a primary component in rechargeable batteries. Nickel is primarily used in the production of stainless steel.

Copper is a good conductor of electricity and it is used for electrical wire, circuit boards, water pipes, and industrial machinery (such as heat exchangers).

Applications in the medical field

Iron and copper are essential metals used in modern medicine. Iron is used to treat or prevent anemia. Copper has been used to treat Wilson's disease and Menkes disease.

The surgical instruments are made of transition metals such as stainless steel, cobalt-chrome alloys, titanium and its alloys. Titanium surgical instruments offer several advantages over stainless steel instruments, such as being lightweight, durable, and corrosion-resistant. Titanium has been used mostly for fabricating dental implants. It is also used in artificial hip bone replacements, and eyeglass frames.

REVIEW QUESTIONS

(1) (a) Name two transition elements used for the building materials.
(b) Most paints contain the compound of a transition element. Why?

(2) (a) Which compound of the transition element is used as the catalyst in the ceramics industry?
(i) scandium (ii) cobalt (iii) vanadium (iv) chromium
(b) Describe two transition elements used for the electroplating.

(3) (a) Why is titanium used in surgical instruments?
(b) Give any two applications for each of the following elements:
(i) manganese (ii) nickel (iii) copper (iv) chromium

Chemistry in Society

- Gemstones are found in different colours due to the presence of transition metal ions. For example, the red colour of ruby is due to a trace amount of chromium. The blue colour of sapphire is due to a trace amount of iron and titanium.
- The coloured compounds of transition elements can be seen in the pottery glazes.
- Transition metals such as iron, chromium, copper, manganese, and zinc are essential trace elements for human beings and plants. They are used in drugs and cosmetic formulations.
- Transition metal complexes have a long history of use as antibacterial and antiviral agents. Copper is used in agriculture as a fungicide (Bordeaux mixture).
- Nichrome wire is an alloy that comes into existence by mixing chromium and nickel. It is used in electric stoves.

EXERCISES

Q 1 to Q 5 (Understanding)

1. Choose the correct answer.
(a) The 3*d* series transition elements contain (10, 9, 8) elements.
(b) The first transition element of the 3*d* series is (nickel, scandium, vanadium).
(c) Copper is a useful transition element because it is (cheap, strong and cheap, strong and a good conductor of electricity).
(d) Transition elements exhibit variable oxidation states because they release electrons from (n*s*, n*p*, (n-1)*d* and n*s*) orbitals.

(e) Titanium is used in dental work because it is (expensive, durable, reactive).

2. Fill in the blanks using the given words:
   Zn; catalysts; coloured; Sc; densities; high; period 4
   The 3*d* series of transition elements run from _____ to _____ of about 10 metals in the _____of the Periodic Table. Most transition elements have _____ melting and boiling points and high _____ compared with the metals in Group I. Transition elements form _____ compounds and most are good _____.

3. Write down the complete electronic configurations of the following:
   (i) Cr^{3+} (ii) Zn^{2+} (iii) Cu (iv) V (v) Co^{2+} (vi) Mn^{2+}
   Given: $_{23}V$, $_{24}Cr$, $_{25}Mn$, $_{27}Co$, $_{29}Cu$, $_{30}Zn$

4. Using the argon core, give the electronic configurations of the following species:
   (i) Cr (ii) Cu^{2+} (iii) V^{2+}
   Given: $_{23}V$, $_{24}Cr$, $_{29}Cu$

5. Give two uses of copper and titanium.

Q 6 to Q 15 (Analysing and Critical Thinking)

6. Which of the 3*d* series transition elements may not be regarded as transition elements by IUPAC definition? Give reasons for your answer.

7. Write down the oxidation states of manganese and also write any two oxides of manganese with different oxidation states. Which one is the most stable oxide?

8. Give the most stable oxidation states for scandium and zinc. Give reasons in terms of electronic configurations.

9. What are the differences between paramagnetic and diamagnetic behaviour?

10. Write the essential electronic configurations of the following transition elements and identify whether these elements are paramagnetic or diamagnetic or ferromagnetic substances.
    (i) $_{24}Cr$ (ii) $_{26}Fe$ (iii) $_{29}Cu$ (iv) $_{30}Zn$

11. Why do transition metals have more oxidation states than other elements?

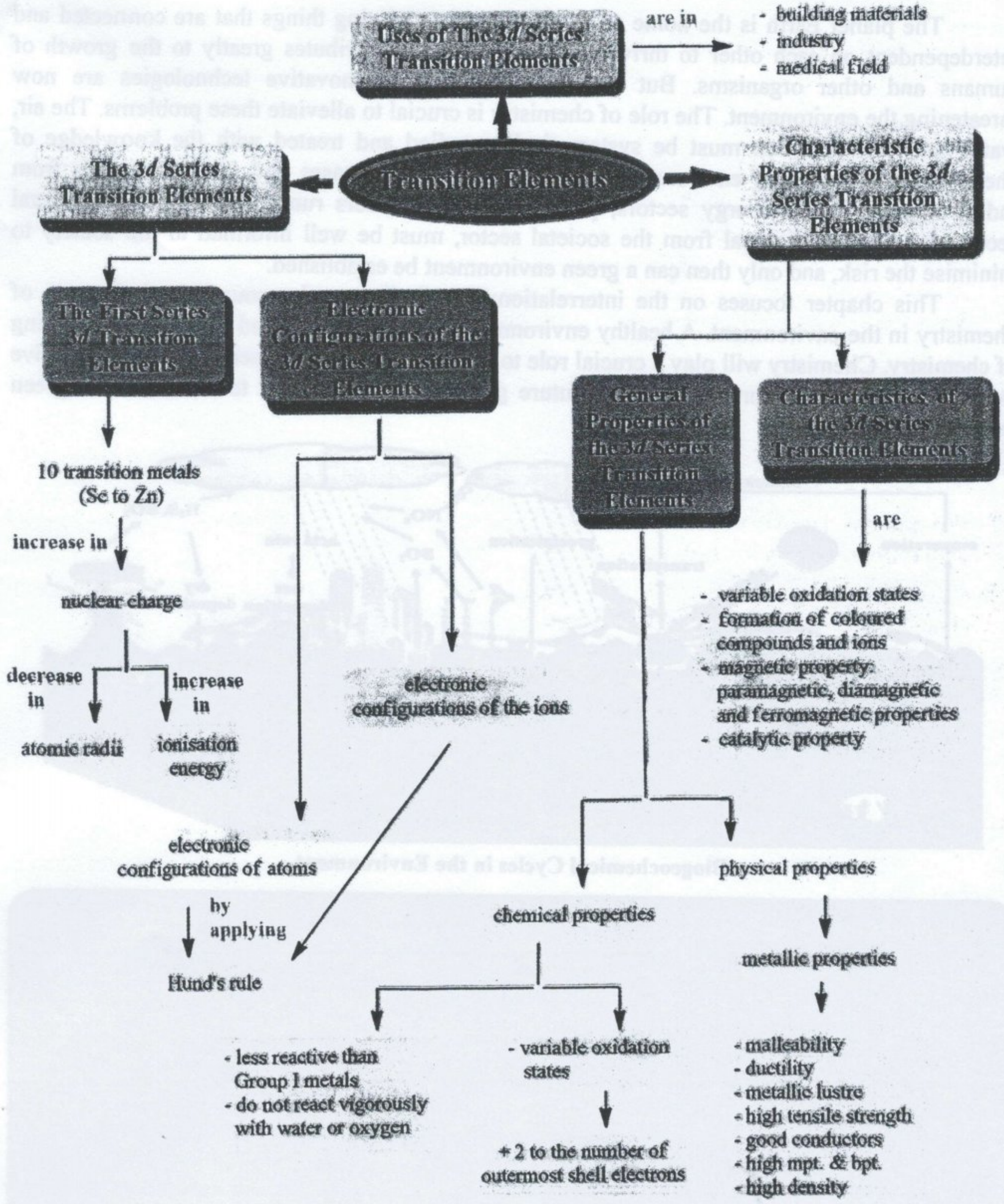
12. Why do titanium surgical instruments are more suitable than stainless steel surgical instruments?

13. Predict the most stable oxidation state in each of the following pairs. Give reasons.
    (i) Cu^{2+} and Cu^{3+} (ii) Ti^{2+} and Ti^{4+} (iii) Fe^{3+} and Fe^{4+} (iv) Co^{3+} and Co^{4+}

14. Explain why transition elements generally form coloured compounds.

15. Why do the electronic configurations of chromium and copper seem to disagree with the regular filling pattern?

CHAPTER REVIEW
(Concept Map)

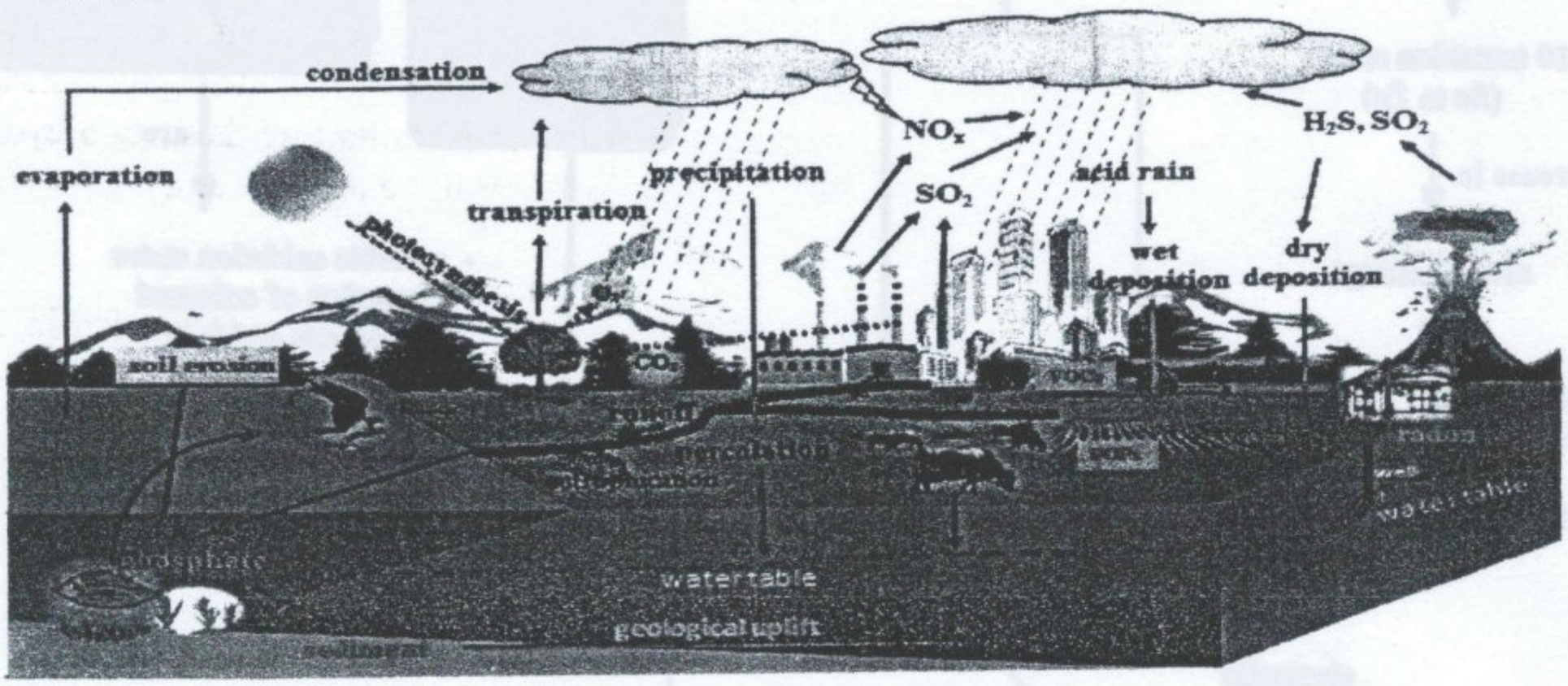


CHAPTER 7

CHEMISTRY AND GREEN ENVIRONMENT

The planet Earth is the home to all living and non-living things that are connected and interdependent on each other to thrive. The environment contributes greatly to the growth of humans and other organisms. But human activities and innovative technologies are now threatening the environment. The role of chemistry is crucial to alleviate these problems. The air, water, and soil pollution must be systematically studied and treated with the knowledge of chemistry. Challenges of environmental issues, such as flue gases and waste materials from industrial and nuclear energy sectors, pesticides and fertilisers runoffs from the agricultural sector, and sewage disposal from the societal sector, must be well informed to the society to minimise the risk, and only then can a green environment be established.

This chapter focuses on the interrelationship of all natural resources and the role of chemistry in the environment. A healthy environment can only be restored by the understanding of chemistry. Chemistry will play a crucial role to understand the consequences of these negative impacts and what measures to take for future green environment and to conserve our green environment.



Biogeochemical Cycles in the Environment

Learning Outcomes

After completing this chapter, students will be able to:

- discuss the biogeochemical cycles of carbon, nitrogen, phosphorus and sulphur;
- explain how human activities have impacted these cycles and the resulting potential consequences for the Earth;
- investigate the hazardous substances present in the environment;
- categorise the impacts of pollutants on the environment;
- describe the sources of radioactive substances and their usefulness;
- identify the pros and cons of radioactivity and radioactive substances;
- describe the green techniques to minimise environmental pollution.

7.1 OUR ENVIRONMENTAL WORLD

The environment is the surroundings comprising of hydrosphere, lithosphere, atmosphere and biosphere. The flora and fauna operate in the dynamic interaction of climatic factors, living things and natural resources for survival and progress of all well-being. Both natural and man-made chemical substances in the environment have a direct impact on human survival and development. In this context, all the chemical reactions that take place in the environment are directly related to the natural matter cycling and transformation of the elements on the Earth.

(a) Natural Matter Cycling

In the natural matter cycling, carbon, nitrogen, oxygen, phosphorus, and sulphur take a variety of chemical forms and may exist for a long period in the atmosphere, on land, in water or beneath the Earth's surface. The pathways that allow different chemical substances to move through living and non-living forms and their locations in the biosphere are called a **biogeochemical cycle**.

The cycling of elements is interconnected with the water cycle. For example, water runoff is critical for leaching nitrogen and phosphate into rivers, lakes, and oceans. The ocean is also a major reservoir for all soluble or insoluble substances. Thus, mineral nutrients are cycled, either rapidly or slowly, through the entire biosphere and from one living organism to another. The detailed description of the natural cycles of carbon and nitrogen is given in the Grade 11 Chemistry Textbook. In this section, the summarised description of these two cycles and the detailed description of the phosphorus and sulphur cycles will be highlighted.

(i) Carbon cycle

Most of the Earth's carbon is stored in rocks and sediments. The rest is located in the ocean, atmosphere, and in living organisms. These are the reservoirs through which carbon cycles.The carbon cycle is the biogeochemical cycle by which carbon is exchanged among the biosphere, geosphere, hydrosphere, and atmosphere of the Earth. The processes involved in the carbon cycle are photosynthesis, respiration, exchange, fossilisation, sedimentation, and combustion (Figure 7.1).

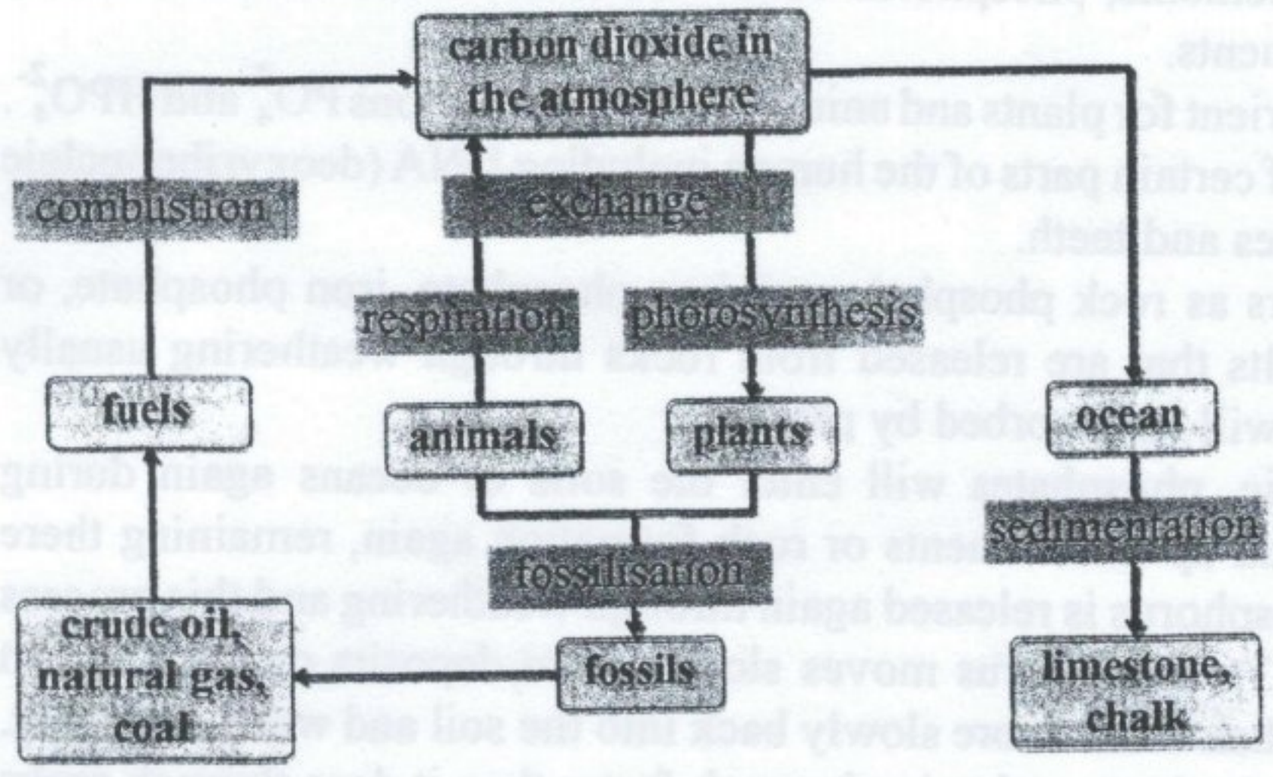


Figure 7.1 Carbon Cycle in the Environment

Plants constantly exchange carbon with the atmosphere. They absorb carbon dioxide during photosynthesis. Plants then release carbon dioxide when they decay. Respiration is the process of gas exchange between the atmosphere and living organisms. Animals exhale carbon dioxide when they breathe. The oceans also obtain carbon from the atmosphere by absorbing carbon dioxide. In the fossilisation process, the animal and plant residues become sediment and eventually turn into rock and minerals. The carbon is stored as coal and other fossil fuels in rocks and other geological deposits. The combustion of fossil fuels and organic materials gives off carbon dioxide, water, and energy.

(ii) Nitrogen cycle

The nitrogen cycle is a biogeochemical process through which nitrogen is converted into many forms, consecutively passing from the atmosphere to the soil and then to organisms, and back into the atmosphere. The nitrogen cycle involves the following steps: nitrogen fixation, nitrification, nitrogen assimilation, ammonification, and denitrification (Figure 7.2).

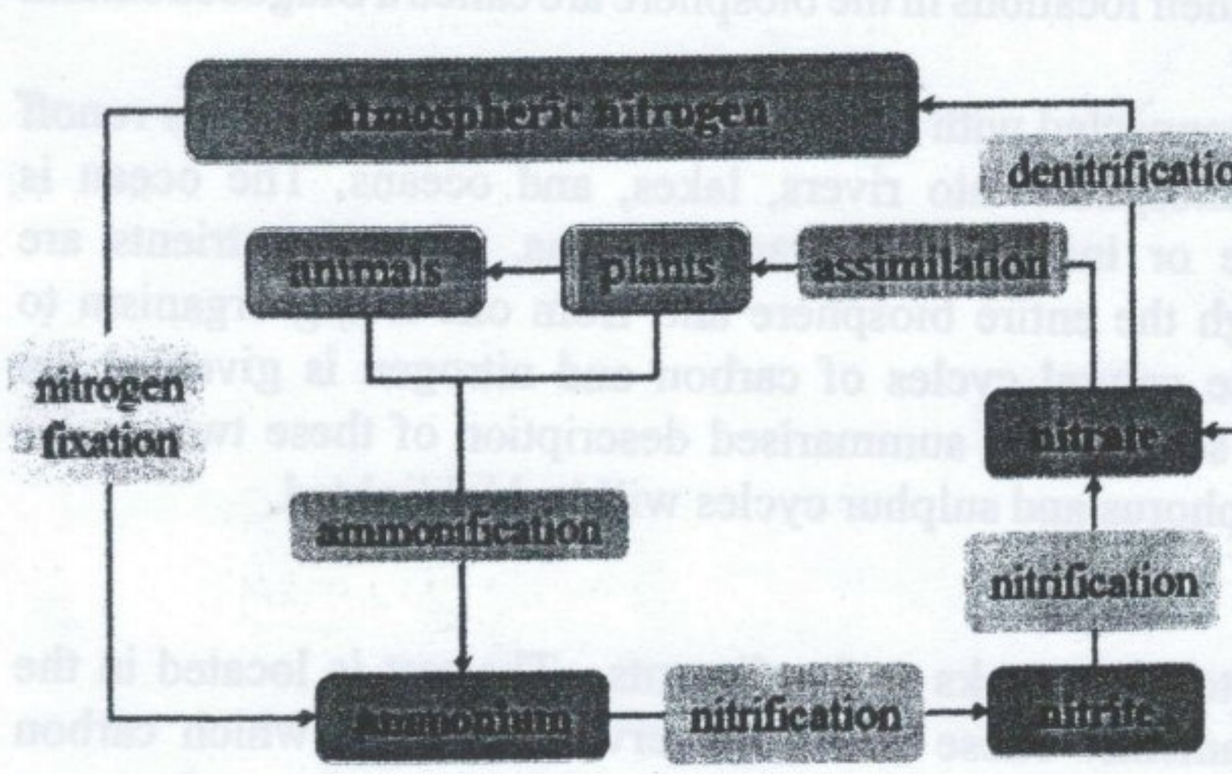


Figure 7.2 Nitrogen Cycle in the Environment

The detailed description of the nitrogen cycle has been expressed in Section 7.1(c), the Grade 11 Chemistry Textbook.

(iii) Phosphorus cycle

Unlike many other cycling elements, phosphorus cannot be found in the air. It is mainly cycling through water, soil and sediments.

Phosphorus is an essential nutrient for plants and animals in the form of ions PO_4^{3-} and HPO_4^{2-}. Phosphorus is also a building block of certain parts of the human including DNA (deoxyribonucleic acid) and animal bodies, such as bones and teeth.

In the soil, phosphorus occurs as rock phosphate, calcium phosphate, iron phosphate, or aluminium phosphate. Phosphate salts that are released from rocks through weathering usually dissolve in water present in soil and will be absorbed by plants.

When animals and plants die, phosphates will enter the soils or oceans again during decay. After that, phosphorus will end up in sediments or rock formation again, remaining there for millions of years. Eventually, phosphorus is released again through weathering and this process proceeds in a cyclic way (Figure 7.3). Phosphorus moves slowly from deposits on land and in sediments, to living organisms, and then much more slowly back into the soil and water sediment. **The phosphorus cycle** moves through plants and animals much faster than it does through rocks and sediments.

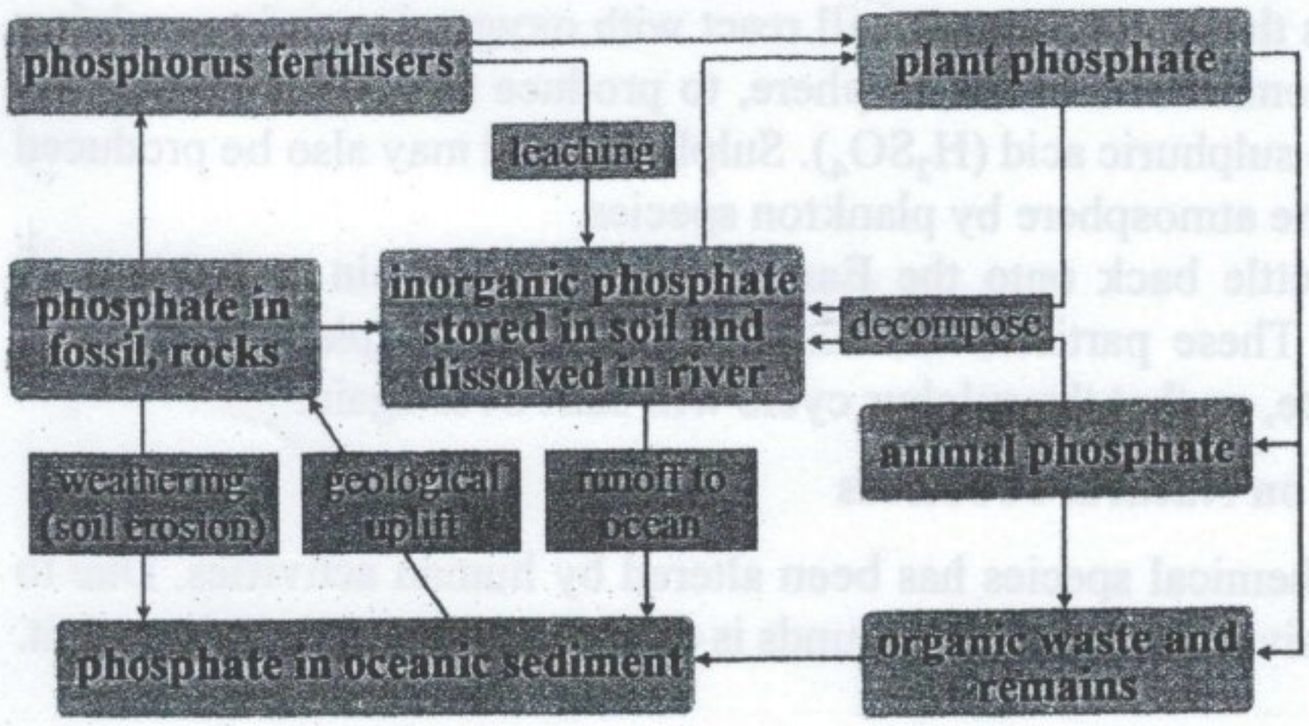


Figure 7.3 Phosphorus Cycle in the Environment

Marine birds play a unique role in the phosphorus cycle, as they take phosphorus-containing fish out of the ocean and return to land, where they defecate. Their guano contains a high level of phosphorus and in this way, marine birds return phosphorus from the ocean to the land.

(iv) Sulphur cycle

The **sulphur cycle** (Figure 7.4) moves through the rocks, water bodies, atmosphere and living systems.

Sulphur is one of the components that make up proteins and vitamins. Plants absorb sulphur when sulphur-containing compounds are dissolved in water. Animals consume these plants, so that they take up enough sulphur to maintain their health.

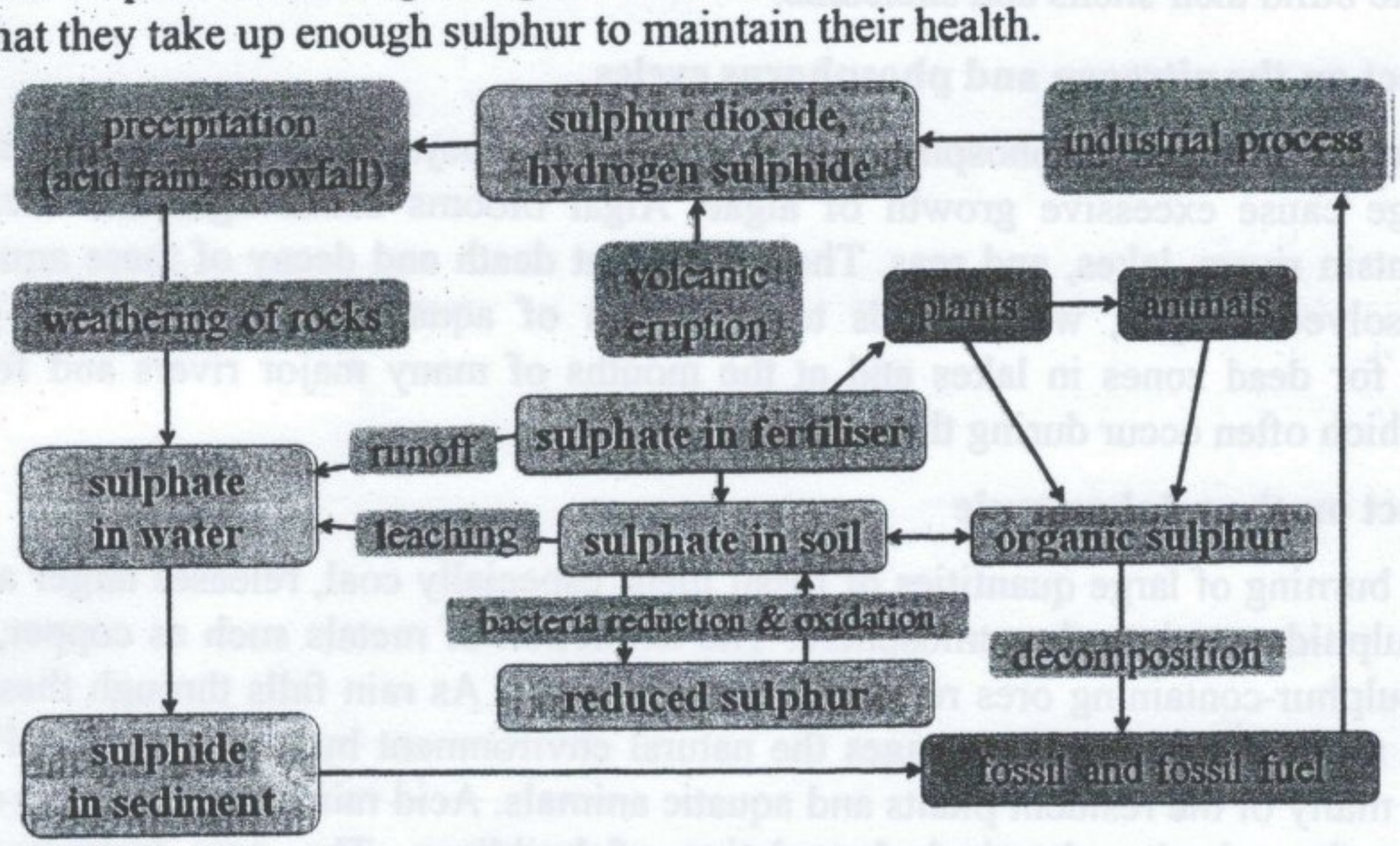


Figure 7.4 Sulphur Cycle in the Environment

Most of the Earth's sulphur is found in rocks and salts or buried deep in the ocean in oceanic sediments. Sulphur can also be found in the atmosphere by entering through both natural and human activities. Natural sources can be, for instance, volcanic eruptions, bacterial processes, or decaying **organisms**. When sulphur enters the atmosphere through human activity, this is mainly a consequence of industrial processes where sulphur dioxide (SO_2) and hydrogen sulphide (H_2S) gases are emitted on a wide scale.

When sulphur dioxide enters the atmosphere, it will react with oxygen to produce sulphur trioxide gas (SO_3), or with other chemicals in the atmosphere, to produce sulphur salts. Sulphur dioxide reacts with water to produce sulphuric acid (H_2SO_4). Sulphuric acid may also be produced from dimethyl sulphide emitted to the atmosphere by plankton species.

All these substances will settle back onto the Earth, or react with rain and fall back onto the Earth as acid deposition. These particles will then be absorbed by plants again and are released back into the atmosphere, so that the sulphur cycle will start over again.

(b) Effect of Human Activities on Natural Processes

The cycling of the natural chemical species has been altered by human activities. Due to the results of these actions, an excessive amount of compounds is discharged into the environment.

(i) Effect on the carbon cycle

Carbon dioxide is released into the atmosphere by animal husbandry practices. A large number of animals raised to feed the Earth's growing human population results in increased carbon dioxide and methane levels in the atmosphere. Human activities have a huge impact on the carbon cycle. Burning fossil fuels, deforestation, changing land use, and using limestone to make concrete transfer significant quantities of carbon into the atmosphere rapidly. The ocean absorbs much of the carbon dioxide that is released from burning fossil fuels. This extra carbon dioxide is lowering the ocean's pH, through a process called **ocean acidification**. Ocean acidification interferes with the ability of marine organisms (including corals, Dungeness crabs, and snails) to build their shells and skeletons.

(ii) Effect on the nitrogen and phosphorus cycles

Excess nitrogen and phosphorus that enter the ecosystem from fertiliser runoff and from sewage cause excessive growth of algae. Algal blooms block light and therefore kill aquatic plantsin rivers, lakes, and seas. The subsequent death and decay of these aquatic plants deplete dissolved oxygen, which leads to the death of aquatic organisms. This process is responsible for dead zones in lakes and at the mouths of many major rivers and for massive fish kills, which often occur during the summer.

(iii) Effect on the sulphur cycle

The burning of large quantities of fossil fuels, especially coal, releases larger amounts of hydrogen sulphide gas into the atmosphere. The extraction of metals such as copper, lead, and zinc from sulphur-containing ores releases sulphur dioxide. As rain falls through these gases, it causes acid rain. This acid rain damages the natural environment by lowering the pH of lakes, thus killing many of the resident plants and aquatic animals. Acid rain also affects the man-made environment through the chemical degradation of buildings. The new technology in the coal-fired power plant is now in use to reduce the release of sulphur dioxide into the atmosphere.

(c) Green Environment

Nowadays, our Earth is facing many environmental issues mainly caused by humans. Many environmental problems like global warming, air pollution, waste disposal, water pollution, climate change and many more are affecting every living and non-living thing on the Earth. To sustain the natural environment and to develop our world, the best way is to make a clean and green environment. A green environment will promote good health.

The clean and green environment implies the absence of pollution and a better quality of life. This includes supporting practices like informed consumption, conservation practices and investment in renewable energy. Green technology is an environmentally friendly technology that builds products and systems to conserve natural resources and the environment. It is applied in green chemistry. Thus, green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. A green synthesis which is used in green chemistry also helps reduce harmful gas emissions, conserve water, reduce waste and utilise less consumption of energy. The 7 R's of a green environment for sustainable development are Rethink, Refuse, Reduce, Reuse, Repair, Regift, and Recycle.

REVIEW QUESTIONS

(1) List the main biogeochemical cycles. Among them, which cycle does not involve the atmosphere?

(2) (i) Name the processes involved in the carbon cycle.
(ii) Which processes in the carbon cycle play a major role in the survival for plants and animals?
(iii) What gases evolve from the burning of coal that causes environmental problems?

(3) What are the 7 R's of the green environment?

Key Terms

- **Biogeochemical cycle** is any of the natural pathways by which essential elements of living matter are circulated.
- **Phosphorus cycle** is the biogeochemical cycle that describes the movement of phosphorus through the lithosphere, hydrosphere, and biosphere.
- **Sulphur cycle** is a biogeochemical cycle in which the sulphur moves between rocks, waterways, atmosphere and living systems.
- **Organisms** are living biological entities, such as animals, plants, fungi, or bacteria.
- **Ocean acidification** refers to a reduction in the pH of the ocean over an extended period of time, caused primarily by the uptake of carbon dioxide from the atmosphere.

7.2 POLLUTANTS AND IMPACTS ON THE ENVIRONMENT

Environmental pollution is caused by the harmful disposal of substances into the environment. These substances can cause a negative impact on biodiversity, ecosystems, and human health. This section will mainly focus on harmful substances such as some heavy metals, pesticides, persistent organic pollutants, and volatile organic compounds.

(a) Heavy Metals and Their Compounds

Heavy metals are metals with high density and toxic effects even at very low concentrations. The utilisation of heavy metals and their compounds by humans influences the potential for health effects in at least two major ways: first, by environmental transport, that is, by human or anthropogenic contributions to air, water, soil, and food, and second, by altering the biochemical form of the elements. Arsenic, cadmium, lead and mercury and their compounds are described in this section.

Arsenic and their compounds

Pure arsenic is rarely found in nature and is not very toxic, but it can be oxidised easily in humid air and becomes toxic by conversion to arsenic anhydride. Arsenic is mostly found in the form of +3 and +5 oxidation states but is not in elemental form in nature.

The desorption and dissolution of arsenic from arsenic rich rocks and minerals are the main sources of groundwater contamination and soil. After that, this dissolved arsenic contaminates the environment.

Compounds such as calcium arsenide, lead arsenide and sodium arsenate, which are highly water soluble, are used for the production of paint (green, yellow), glass, ceramics, and semiconductors. Sodium arsenate is used to kill some parasites in fruit cultivation and potato growing.

Arsenic compounds cause acute and chronic effects in individuals, communities and populations at concentrations ranging from a few micrograms to milligrams per litre, depending on species, and time of exposure.

Cadmium and their compounds

Cadmium is released into the atmosphere predominantly as elemental cadmium and cadmium oxide from some sources as cadmium sulphide (from coal combustion) or cadmium chloride (from waste incineration). Cadmium exists as the +2 oxidation state in nature. Levels of cadmium in water, air and soil are increasing particularly in industrial areas. Tobacco smoking is also a significant source of cadmium exposure.

Various salts of cadmium are commonly used in electronic cells, accumulators, porcelain, nuclear materials, amalgam in dentistry, plastic, metal coating, vacuum tubes, and photovoltaic materials.

Cadmium in the environment is also toxic to plants, animals and microorganisms.

Lead and their compounds

Lead and its derivatives are industrial toxic substances that have been widely used by humans for centuries. In the environment, lead primarily exists in the +2 and +4 oxidation states.

Lead enters the atmosphere largely in the exhaust fumes from internal combustion engines. Consequently, the lead content of the air is the highest in urban industrial areas and the lowest in rural areas.

The primary use of lead is in the manufacture of batteries, and in the production of paint, alloys and metal products in the industry. An increased level of lead in the environment can result in decreased growth and reproduction in plants and animals, and neurological effects in vertebrates.

Mercury and their compounds

Elemental mercury occurs in nature. Mercury can also be found in +1 and +2 oxidation states.

Mercury is released into the environment from a variety of sources, both natural and anthropogenic. Inorganic mercury can be transformed into methylmercury by microorganisms such as phytoplanktons and fungi. It then bioaccumulates in fish and shellfish.

The source of exposure to low levels is mercury released from amalgam from the panning of gold and fillings in teeth. It is generally taken into the body in the form of vapour. Mercury

may have toxic effects on the nervous, digestive and immune systems, and on the lungs, kidneys, skin, eyes, and development of the child in utero and early in life.

(b) Pesticides

A pesticide is a substance that kills a pest, or it prevents or reduces the damage a pest may cause. Pests can be insects, mice or other animals, unwanted plants (weeds), fungi, bacteria or viruses.

Pesticides are often grouped into "families" because they act on the pest in the same way. Some common families include organophosphates, organochlorines, carbamates and thiocarbamates, and pyrethroids.

Many processes affect what happens to pesticides in the environment. These processes include adsorption, transfer, and degradation. Adsorption occurs because of the attraction between a chemical and soil particles. Positively charged pesticide molecules, for example, are attracted to and can bind to negatively charged clay particles. Many soil factors influence pesticide adsorption. The transfer includes processes that move the pesticide away from the target site. These include volatilisation, spray drift, runoff, leaching, absorption and crop removal. Degradation is the process of pesticide breakdown after application. Pesticides are broken down by microbes, chemical reactions, and **photodegradation**. This process may take anywhere from hours or days to years, depending on environmental conditions and the chemical characteristics of the pesticides.

Pesticides can contaminate soil, water, turf, and other vegetation. In addition to killing insects or weeds, pesticides can be toxic to a host of other organisms including birds, fish, beneficial insects, and non-target plants. Pesticides can cause short-term adverse health effects, called acute effects, as well as chronic adverse effects that can occur months or years after exposure.

(c) Persistent Organic Pollutants (POPs) and Volatile Organic Compounds (VOCs)

Persistent organic pollutants (POPs) and **volatile organic compounds** (VOCs) are two of the most insidious forms of toxic contamination.

POPs are also carbon-based organic compounds that have the special abilities to be long-lasting and to resist breakdown into safer substances. They include industrial chemicals like polychlorinated biphenyls (PCBs) and pesticides like dichlorodiphenyltrichloroethane (DDT). POPs are primary products and by-products from industrial processes, chemical manufacturing and resulting wastes.

POPs are chemically stable, remain intact in the environment for long periods, and are lipophilic in nature. Therefore, they accumulate in the fatty tissue of living organisms and reside for a longer period of time finally affecting humans and wildlife.

VOCs are organic chemicals that pollute the air and be absorbed or inhaled by humans, animals and plants. They are generally man-made carbon-based molecules such as paint thinners, dry cleaning fluid, nail polish remover, grease solvents and the emissions of crude oil, fuels and plastics. VOCs play a significant role in the formation of ozone and fine particulates in the atmosphere. Under sunlight, VOCs react with nitrogen oxides emitted mainly from vehicles, power plants and industrial activities to form ozone, which in turn helps the formation of fine particulates. The accumulation of ozone, fine particulates and other gaseous pollutants results in smog that reduces visibility.

The burning of plastics releases toxic gases like dioxins, furans, mercury and polychlorinated biphenyls into the atmosphere, and poses a threat to vegetation, and human and animal health.

REVIEW QUESTIONS

(1) Classify the pollutants given below as inorganic and organic substances.
sodium arsenate; DDT; methylmercury; lead; cadmium sulphide; PCBs

(2) Which mercury compound can accumulate in the body of living things? Describe the toxic effects of mercury on humans.

(3) (a) Describe the ways to break down a pesticide.
(b) Give one example each for POPs and VOCs.

Key Terms

- **Photodegradation** is a process by which substances are broken down by the action of sunlight.
- **Persistent organic pollutants** (POPs) are carbon-based organic compounds that have the special abilities to be long-lasting and to resist breakdown into safer substances.
- **Volatile organic compounds** (VOCs) are organic chemicals that can vaporise.

7.3 RADIOACTIVE SUBSTANCES AND THE ENVIRONMENT

Radioactive substances include radioactive material radioisotopes, and radioactive waste. Radioactive pollution is the result of released radionuclides in the environment. A radionuclide is an atom with an unstable nucleus which has excessive energy.

(a) Radioactivity

Radioactivity is a spontaneous process of decay or disintegration of heavy nuclei generating different types of radiation such as alpha particles, beta particles and gamma rays, and forming a new element(s). These radiations including X-rays are called ionising radiation.

The penetrating power of alpha particles, beta particles, and gamma rays varies greatly (Figure 7.5). Alpha particles can be blocked by a few pieces of paper. Beta particles pass through paper but are stopped by aluminium foil. Low energy beta particles may penetrate the superficial layer of skin, whereas high energy beta particles will penetrate the skin a centimetre or more. Gamma rays are the most difficult to stop and require concrete, lead, or other heavy shielding to block them. Gamma rays and X-rays can cause severe damage to the cell.

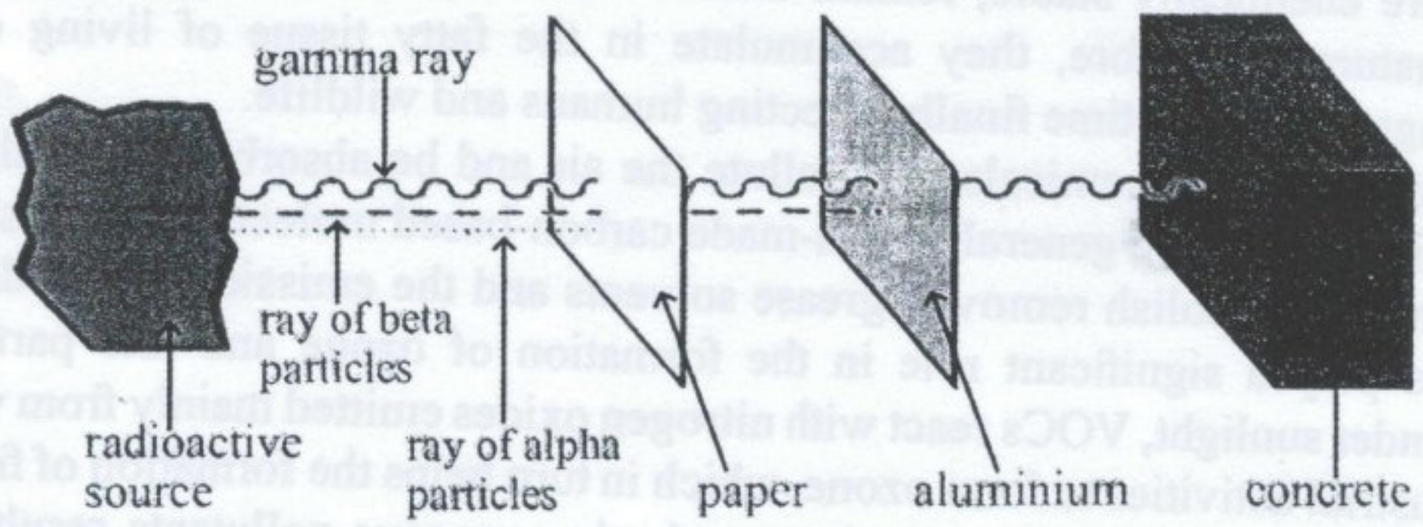


Figure 7.5 Penetrating Power of Three Types of Radiation

(b) Some Radiation Sources

The majority of **background radiation** occurs naturally from minerals and a small fraction comes from man-made elements. Naturally occurring radioactive minerals in the ground, soil, and water produce background radiation. The human body even contains some of these naturally occurring radioactive minerals. Cosmic radiation from space also contributes to the background radiation around us. Hence, radiation is all around us.

(i) Radioactive substances on the Earth and in the bodies

A trace amount of radionuclides, uranium and thorium, are naturally found on the Earth. Traces of radioactive materials can be found in the body, mainly naturally occurring potassium-40. It is found in the food, and water we ingest. The radioactive gas, radon, can be found at higher levels in the air in houses and other buildings, as well as in water from underground sources. Prolonged exposure to radon gas can cause lung cancer.

(ii) Man-made sources

Uranium-235, americium-241, and plutonium-239 are fissile materials produced from a breeder reactor. Hydrogen-3 (tritium), cobalt-60, iodine-129, caesium-132, and barium-137 are man-made radiation sources. A small fraction of background radiation comes from human activities. Ionisation smoke detectors use americium-241 as a source of alpha particles. Alpha particles from the americium source ionise air molecules. There is no health threat from ionisation smoke detectors as long as the detector is not damaged and used as directed.

Radioactive materials used in industry and even in some consumer products and healthcare are a source of small amounts of background radiation.

(c) Uses of Radioisotopes

The applications of radioisotopes have played a significant role in improving the quality of life of human beings. Radiotracers are widely used in medicine, agriculture, food preservation and sterilisation, industry and civil engineering, and fundamental research. Radiotracer is a radioactive isotope used to study the dynamic behaviour of various chemical and biological changes in a system.

A well-known use of carbon-14 is radiocarbon dating which can be used to date wooden and organic objects, especially in archaeology. Moreover, uranium-235 is used as fuel for nuclear power plants and naval nuclear propulsion systems. Caesium-137 is used as a tracer in medical radiation therapy devices for treating cancer, and in industrial gauges that detect the flow of liquid through pipes.

(d) The Nuclear Power and Nuclear Weapons

Nuclear reactors generate electricity and are used in nuclear marine propulsion. These reactors use **fissile heavy atoms** (^{233}U, ^{235}U, ^{239}Pu) as fuel instead of fossil fuels. Radioactive nuclides such as plutonium-239 or uranium-235 are commonly used in nuclear reactors and nuclear bombs.

Nuclear bombs are weapons having massive destructive power. The explosion of a nuclear weapon releases a combination of heat, blast waves and radiation. These forces have radiation

causes massive destruction of buildings and infrastructures. Severe consequences on the environment last for many years.

(e) Impact of Radioactive Substances on the Environment

Radionuclides found in water are potassium-40, radium-226 and radium-228. These isotopes originate from natural sources due to leaching from minerals. Water bodies are also polluted by accidental leakage of waste material from uranium and thorium mines, nuclear power plants and industries.

Radioactive materials can enter the human body through water and food and may be accumulated in blood and certain vital organs. They cause tumours and cancer.

REVIEW QUESTIONS

(1) Which particles or rays are emitted from a radioactive substance? What is the penetrating power for each emitted particle or ray?

(2) What is the usefulness of the following radionuclides?
carbon-14; caesium-137; uranium-235; americium-241

(3) Choose the fissile nuclides from the following:
Co-60, I-129, U-233, Pu-239, Ba-137

Key Terms

- **Radioactivity** is the process by which the nucleus of an unstable atom loses energy by emitting radiation, including alpha particles, beta particles, and gamma rays.
- **Background radiation** is a measure of the level of ionising radiation naturally present in the environment at a particular location.
- **Fissile heavy atoms** are materials capable of sustaining a nuclear fission chain reaction.

7.4 CHEMISTRY FOR SUSTAINABLE ENVIRONMENTAL DEVELOPMENT

Chemistry plays an essential role to achieve the United Nations Sustainable Development Goals. Chemistry offers a wide range of products and processes essential to our daily lives that are safe, sustainable, and environmentally sound. As mentioned in Section 7.1 (c), some principles that reduce or eliminate the use of hazardous substances in the design, manufacture and application of chemical products to minimise environmental pollution are especially highlighted in green chemistry.

(a) Agricultural Sector

The agricultural sustainability is the area that requires green chemistry strategies in the manufacturing of agrochemicals due to their direct impact on human and environmental health. Nowadays, organic farming that uses fertilisers of organic origin such as compost manure, green manure, and bone meal instead of chemical fertilisers may be one way or another to minimise the environmental problems. Additionally, instead of using chemical-based pesticides, plant-based pesticides that have minimum risks including essential oils and insecticidal soaps can be used.

Plant-based pesticides

These pesticides are safer than chlorinated hydrocarbons. For instance, the neem leaves consist of insecticidal ingredients and they can be used as an insecticide. To provide nutrients in a plant-available form, agrochemists have developed formulation technology to produce plant-based pesticides . These plant-based pesticides vastly improve the fraction of nutrients in fertilisers absorbed by plants, significantly reduce fertiliser application rates, and minimise runoff to nearby surface water. Generally, a plant-based pesticide forms a stable water soluble complex with nutrient molecules to prevent mineralisationin the soil and facilitate foliar application directly to the leaves.

Plant-based insecticidal soaps

Plant-based insecticidal soaps can be used either on indoor plants or on outdoor plants, including vegetables to eliminate small soft-bodied insects. Insecticidal soaps have several advantages over pesticides in that they leave no nasty residue, are non-toxic to animals and birds, and do not harm beneficial insects.

(b) Energy Sector

Some major themes in the green societal sector today include reducing our reliance on non-renewable energy sources.

(i) Transformation of solid wastes to greener fuels

The municipal and non-hazardous industrial wastes have been converted to energy by direct burning. This process is known as waste gasification or pyrolysis.

In this method, much of the organic content wastes in the reactor produce a mixture of hydrogen and carbon monoxide. The gas mixture is sent to a catalytic system that converts it to ethanol and methanol or other liquid fuels or chemicals. Vegetables and other waste materials can also be used to produce greener fuels.

(ii) Renewable energy resources

Solar, wind, hydroelectric, biomass, biorefineries, geothermal, and tidal energy are important resources for future sustainable development, so they will replace carbon-containing sources (fossil fuels) and reduce the emission of greenhouse gases.

(iii) Biofuels

Chemists are now researching new methods that are more environmentally friendly and sustainable. It can be obtained from biomass which is coming from sugar cane, rapeseed, corn, straw, wood, animal and agriculture residues. The production of bioethanol and biodiesels will be highlighted for the production of biofuels.

Bioethanol

Ethanol is the most important alcohol which can be produced by converting the sugar content of anystarchy material into alcohol with the evolution of carbon dioxide (CO_2) under controlled environmental condition. Productions of ethanol are from lignocellulosic materials such as corncob, cornstalk, cornhusk, sugarcane bagasse and sugarcane bark.

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{yeast}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

Biodiesel

Many vehicles around the world are fueled with diesel oil, and the production of **biodiesel** oil is a promising possibility. Biodiesel oil is produced from cultivated plant oil. It is synthesised from plant oils by removing the by-product glycerine molecule, valuable raw material for soap production.

Biodiesel oil also can be obtained from waste plant oils, e.g., oils used in restaurants. In the technological process, potential waste is transformed into valuable fuel. The combustion of fossil fuel generates sulphur compounds whereas biodiesel does not.

(c) Wastewater Treatment

Nowadays, water contamination is increasingly an important issue in developing and under developed countries. Many clean water resources are becoming increasingly scarce and many of them are polluted by anthropogenic sources such as industrial purposes, agricultural waste and household. Therefore, the treatment of wastewater is a critical need. The main purpose of wastewater treatment is to remove the various contaminants that are present in the wastewater namely suspended solids, organic carbon, nutrients, inorganic salts, heavy metals and pathogens.

The green materials such as agricultural waste adsorbent, activated carbon, and rice husk-derived ceramic materials are usually applied in the wastewater treatment system. Moreover, the photocatalysts binary metal oxides nanomaterials (e.g., TiO_2, ZnO, Fe_2O_3) are also used to mineralise, decompose, and oxidise the pollutants from wastewater.

(d) Consumer Goods in Societal Sector

Some eco-friendly materials used in consumer goods are given in this section.

Unleaded petrol

Previously, tetraethyllead (TEL) was used as an anti-knocking agent. Nowadays, it is replaced by using methyl *tert*-butyl ether (MTBE). It is a flammable liquid that has been used as an additive for unleaded petrol. Thus, it reduces air pollutant emissions.

Bioplastics

Bioplastics are derived from renewable biomass sources such as corn starch, vegetable oils and fats. It is used for disposable items such as packaging, pots, crockery, bowls, etc.

Daily life chemicals

Solvents like tetrachloroethene ($Cl_2C{=}CCl_2$) used in dry cleaning of clothes, pollute the groundwater and are carcinogenic.

In the liquid CO_2 cleaning process, liquid carbon dioxide and other non-toxic cleaning materials replace tetrachloroethene. Dry cleaners pressurise and then liquefy CO_2 gas to make it a powerful solvent for cleaning clothing items. After the dry-cleaning process, the CO_2 gas is safely stored in a storage tank for reuse. Although the liquid CO_2 cleaning process requires expensive and special machines, it effectively reduces the environmental problems.

(e) Industrial Sector

For reducing the environmental pollution in the industrial sector, **green chemistry**, also called sustainable chemistry, can design chemical products and processes that reduce or

eliminate the use or generation of hazardous substances. Examples of green processes used in industries are given below.

Green synthesis of adipic acid

Large amounts of adipic acid, $HOOC(CH_2)_4COOH$, are used each year for the production of nylon, polyurethanes, lubricants and plasticisers. Benzene, a compound with convinced carcinogenic properties, is a standard substrate for the production of this acid.

Chemists developed a green synthesis of adipic acid using a less toxic substrate. Furthermore, the natural source of this raw material, glucose, is almost inexhaustible. Glucose can be converted into adipic acid by an enzyme discovered in genetically modified bacteria. Such a manner of production of this acid guards the workers and the environment against exposure to hazardous chemical compounds.

Chromium plating

Hexavalent chromium plating is the method of chromium plating (most commonly known as chrome plating) and can be used for decorative and functional finishes. This type of plating produces several by-products which are considered as hazardous waste, including lead chromates and barium sulphate. Hexavalent chromium itself is a hazardous substance and carcinogen.

Trivalent chromium is another method of decorative chrome plating, and is considered as an environmentally friendly alternative to hexavalent chromium, with many of the same characteristics; just like hexavalent chrome finishes, trivalent chrome finishes provide scratch and corrosion resistance and are available in a variety of colour options. Trivalent chromium plating uses chromium sulphate or chromium chloride as its main ingredient, instead of chromium(VI) oxide; making trivalent chromium less toxic than hexavalent chromium.

REVIEW QUESTIONS

(1) What are the fuel products produced from the waste gasification process?

(2) What are the resources of renewable energy?

(3) What by-product from the biodiesel production can be used as a raw material for the production of soap?

Key Terms

- **Biodiesel** is a form of diesel fuel derived from plants or animals and consisting of long-chain fatty acid esters.
- **Green chemistry** is the design of chemical products and processes that reduce or eliminate the generation of hazardous substances.

Chemistry in Society

- Vermilion is a dense, opaque pigment with a clear, brilliant hue. The pigment was originally made by grinding a powder of cinnabar (mercury(II) sulphide, HgS). It is used as a red pigment in the production of lacquerware.
- Arsenic trisulphide (As_2S_3) is used as orpiment in works of art. The orpiment (orange-yellow As_2S_3) is highly desirable as a pigment mostly in lacquerware because of its bright yellow colour, mimicking that of gold.
- Bananas are naturally high in potassium. Potassium is a mix of isotopes, including the slightly radioactive isotope potassium-40.
- Clove oil (eugenol), mint oil (menthol, pulegone), lemongrass oil (citronellal, citral), cinnamon oil (cinnamaldehyde), rosemary oil (1,8-cineole) and oil of oregano (carvacrol) are the best-known essential oils containing organic compounds (major components are given in the brackets) with bioactivity against insects and other pests.

EXERCISES

Q 1 to Q 5 (Understanding)

1. State TRUE or FALSE for each of the following. If FALSE, correct it.
   (a) The atmosphere is the reservoir of carbon that is most affected as a direct result of human activity.
   (b) Persistent organic pollutants lead to the form of smog.
   (c) Degradation of pesticides can occur before application on the farm.
   (d) Trivalent chromium is more toxic than hexavalent chromium.
   (e) Phosphorus can be found in a gaseous state in the biogeochemical cycle.
2. Fill in the blanks with a suitable word or phrase or symbol as necessary.
   (a) The guano of marine birds contains a high level of _____ .
   (b) Bioplastics are derived from _____ biomass sources.
   (c) _____ can be used to date the antique materials in archaeology.
   (d) The heavy metal used in the manufacture of batteries is _____ .
   (e) Tobacco smoking is a significant source of _____ exposure.
3. Choose the correct term or terms given in the brackets.
   (a) DDT and PCB belong to (VOCs, POPs, BVOCs).
   (b) Arsenic is mostly in the form of (+2, +3, +4) valence in nature.
   (c) Beta particles can penetrate (paper, aluminium foil, concrete block).
   (d) Radiation present in the environment but not produced by humans is called (radiometric radiation, radioactive tracer, background radiation).
   (e) According to green chemistry, the chemical involved in the production must be (non-toxic, toxic, highly toxic).

4. Match each of the items given in List A with the appropriate item in List B.

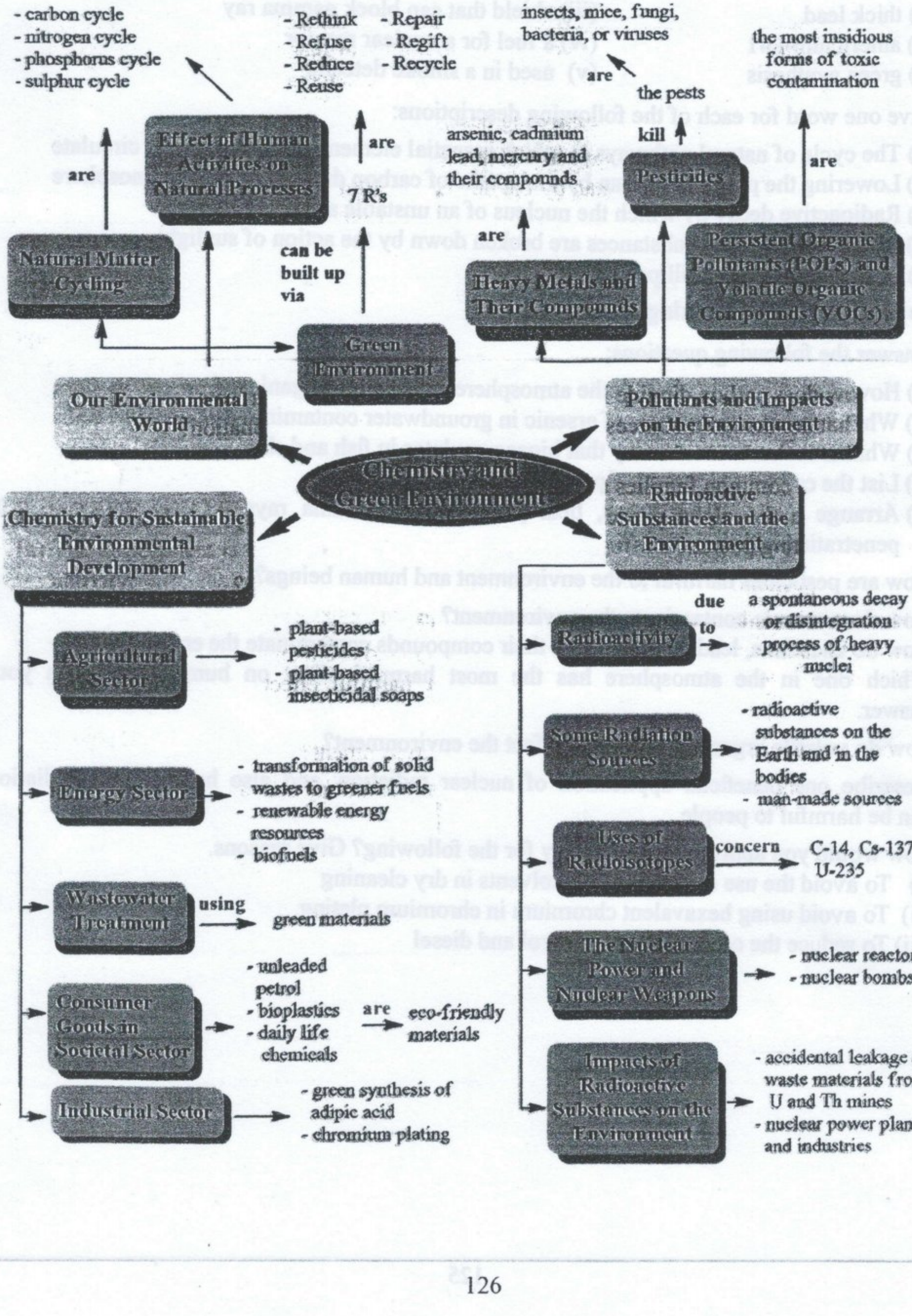
List A	List B
(a) elemental mercury	(i) low energy requirement
(b) uranium-235	(ii) very dense liquid
(c) thick lead	(iii) shield that can block gamma ray
(d) americium-241	(iv) a fuel for a nuclear reactor
(e) green synthesis	(v) used in a smoke detector

5. Give one word for each of the following descriptions:
   (a) The cycle of natural pathways in which essential elements of living matter circulate
   (b) Lowering the pH of the ocean by the uptake of carbon dioxide from the atmosphere
   (c) Radioactive decay by which the nucleus of an unstable atom loses energy
   (d) A process by which substances are broken down by the action of sunlight
   (e) A chemical used to kill pests

Q 6 to Q 12 (Critical Thinking)

6. Answer the following questions:
   (a) How does carbon dioxide in the atmosphere enter living organisms?
   (b) What are the main sources of arsenic in groundwater contamination?
   (c) What is the form of mercury that bioaccumulates in fish and shellfish?
   (d) List the common families of pesticides.
   (e) Arrange the alpha particles, beta particles and gamma rays in decreasing order of penetrating power.
7. How are pesticides harmful to the environment and human beings?
8. How does arsenic contaminate the environment?
9. How do cadmium, lead, mercury, and their compounds contaminate the environment? Which one in the atmosphere has the most harmful effect on humans? Explain your answer.
10. How do volatile organic compounds affect the environment?
11. Describe one beneficial application of nuclear radiation, and also how nuclear radiation can be harmful to people.
12. How would you apply green chemistry for the following? Give reasons.
    (i) To avoid the use of halogenated solvents in dry cleaning
    (ii) To avoid using hexavalent chromium in chromium plating
    (iii) To reduce the consumption of petrol and diesel

CHAPTER REVIEW
(Concept Map)



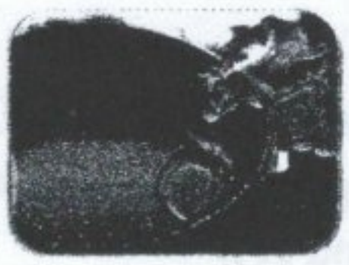
CHAPTER 8

ORGANIC COMPOUNDS AND MACROMOLECULES

The chemical compounds found in living things are referred to as "organic compounds" due to their link with organisms. Organic compounds hold the key to life on the Earth. They make up the majority of our bodies and are also an integral part of our lifestyle. They can be found in the food we eat as well as the clothing we wear. Moreover, medicines, washing powders, dyes, and fossil fuels are made of organic compounds. Additionally, plastics and synthetic fibres, clothes and most other consumer goods contain a significant portion of organic compounds.

The majority of biochemical compounds are big organic molecules that the body uses to carry out numerous biochemical functions. These enormous molecules are termed macromolecules; they are formed by smaller molecules connecting together as if they were holding hands. Carbohydrates, proteins, and nucleic acids are natural polymers, a type of long-chain biological macromolecules. Plastics, fibres, and elastomers, on the other hand, are synthetic macromolecules manufactured in the industry. Some major classes of organic compounds and their reactions, the identification of the functional groups in these compounds, polymerisation and also both addition and condensation polymers are described in this chapter.

Carboxylic acid (in citrus fruits)



Cooking oil and teflon coated pan

Polyester sewing thread

Wood

Shampoo, conditioner and body lotion

PVC pipe

Learning Outcomes

After completing this chapter, students will be able to

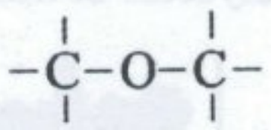
- describe the nomenclature using the IUPAC system, preparation methods, properties and uses of aliphatic organic compounds: ethers, aldehydes, ketones, carboxylic acids, esters, amines and amides;
- classify the organic compounds by using chemical tests;
- identify the functional groups of simple organic compounds by infrared spectroscopy;
- express some natural and synthetic polymers;
- explain the process of polymerisation to show how monomers can combine in polymers;
- describe the chemical nature, reactions, properties and uses of addition and condensation polymers to recognise their importance in society;
- describe the problem of pollution caused by plastics;
- describe how polymers have been designed to act as degradable plastics.

8.1 ORGANIC COMPOUNDS

The simplest organic compounds that contain only the elements carbon and hydrogen are called hydrocarbons, which include aliphatic hydrocarbons (alkanes, alkenes, alkynes) and aromatic hydrocarbons. Many other organic compounds in which carbon atoms are covalently linked to oxygen atoms are alcohols, ethers, aldehydes, ketones, carboxylic acids, and esters. Alcohols can be used as solvents in marker pens, medicines, and cosmetics and as fuels. Ethers can be used as organic solvents in the perfumery and aroma industries. The presence of simple carbonyl compounds is responsible for the pleasant odour of several flowers. The characteristic odour of cherries is due to benzaldehyde. The main component of nail polish remover is acetone. Carboxylic acids are present in many common household items such as vinegar (acetic acid), aspirin (a derivative of salicylic acid), vitamin C (ascorbic acid), and lemons (citric acid). Esters, with aromatic odours, are used in fragrances, essential oils, food flavourings, cosmetics, and other products. Some other organic compounds contain nitrogen atoms, such as amines and amides. Amines are also found in many molecules essential to life, such as amino acids, hormones, and DNA. Nylon and paracetamol are examples of amides. In this section, aliphatic organic compounds - ethers, aldehydes, ketones, carboxylic acids, esters, amines and amides will be studied.

(a) Ethers

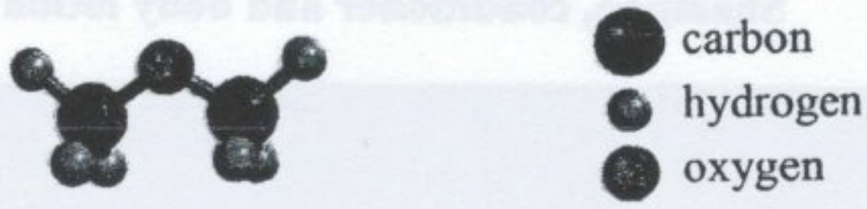
An ether is an organic compound with an O atom bonded to two alkyl groups. In a symmetrical ether, the two alkyl groups are the same (R and R). In an unsymmetrical ether, the two alkyl groups are different (R and R').



R–O–R
symmetrical ether

R–O–R'
unsymmetrical ether

Ethers have the general formula $C_nH_{2n+2}O$. The illustration shows the ball-and-stick model of the simplest ether, dimethyl ether (CH_3OCH_3).



(i) Nomenclature

Ethers are often called by their common names.
For common names, the two alkyl groups connected to the oxygen atom are named separately and followed by "ether".

In the IUPAC system, the oxygen atom and the smaller alkyl group are named as an alkoxy substituent, and the rest of the molecule is named as an alkane.

	$H_3C–O–CH_3$	$C_2H_5–O–CH_3$	$C_2H_5–O–C_2H_5$
Common name:	dimethyl ether	ethyl methyl ether	diethyl ether
IUPAC name:	methoxymethane	methoxyethane	ethoxyethane

(ii) Methods of preparation

Dehydration of alcohols

Ethers can be obtained from alcohol by the elimination of a molecule of water from two molecules of alcohol. For example, when ethanol is treated with a limited amount of sulphuric acid and heated to 140 °C, ethoxyethane (diethyl ether) and water are formed.

$$\underset{\text{ethanol}}{C_2H_5OH} + \underset{\text{ethanol}}{C_2H_5OH} \xrightarrow[140\ ^\circ C]{H_2SO_4} \underset{\text{ethoxyethane}}{C_2H_5OC_2H_5} + H_2O$$

(iii) Properties and uses

Methoxymethane and methoxyethane are colourless gases at room temperature. The other lower homologues are colourless, volatile liquids with the typical smell of ether.

There is no intermolecular hydrogen bonding between ether molecules, which makes their boiling points much lower than alcohol of similar molecular mass. Ethers with up to three carbon atoms are soluble in water and the solubility decreases as the number of carbon atoms increases.

Reaction with hydrogen iodide

On heating with concentrated hydrogen iodide (HI), the C−O bond in ethers breaks forming alcohol and alkyl iodide. For example,

$$\underset{\text{methoxymethane}}{CH_3{-}O{-}CH_3} + HI \xrightarrow{\Delta} \underset{\text{methyl iodide}}{CH_3I} + \underset{\text{methanol}}{CH_3OH}$$

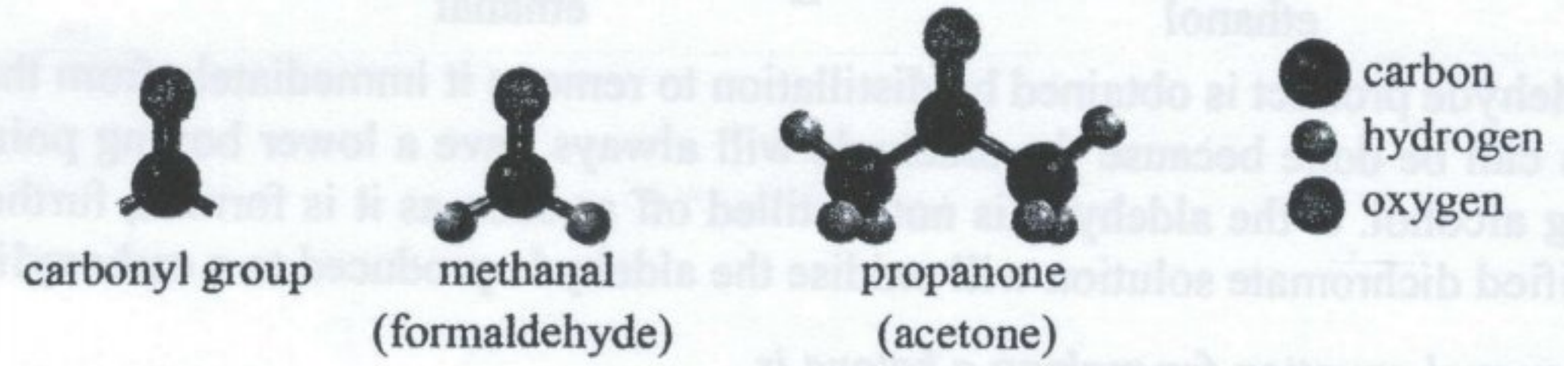
Uses of ethers

They are fairly inert and so they are often used as reaction solvents. Ethoxyethane (diethyl ether), the most common member of the ether family, was used for many years as a surgical anaesthetic agent but has now been replaced by safer nonflammable alternatives.

(b) Aldehydes and Ketones

Aldehydes and ketones are organic compounds which contain the carbonyl group, >C=O. In aldehydes, a carbonyl group located at the end of a carbon chain is bonded to at least one hydrogen atom. In ketones, a carbonyl group can be located within a carbon chain rather than at the end.

Aldehydes and ketones have the general formula $C_nH_{2n}O$ and form a homologous series. The illustrations show the ball-and-stick models of the carbonyl group, the simplest aldehyde, methanal (HCHO) and the simplest ketone, propanone (CH_3COCH_3).



carbonyl group — methanal (formaldehyde) — propanone (acetone)

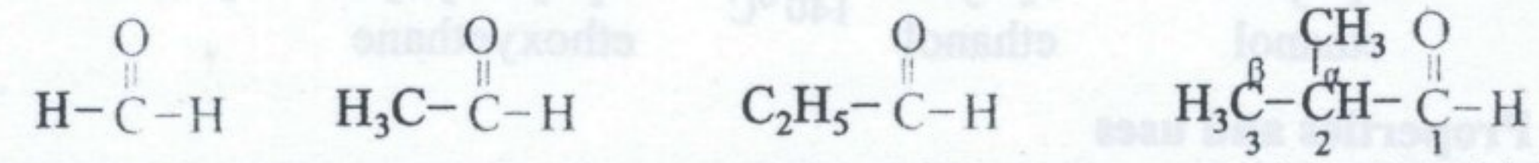
(i) Nomenclature

Aldehydes and ketones are often called by their common names.

The common names of aldehydes are given based on the names of corresponding carboxylic

acids: formaldehyde, acetaldehyde, and so on. The location of the substituent in the carbon chain is indicated by the Greek letters α, β, γ, δ, and so on. An alpha (α) carbon is a carbon atom bonded to a functional group; the beta (β) carbon is next to the α carbon, and so on (γ, δ,...).

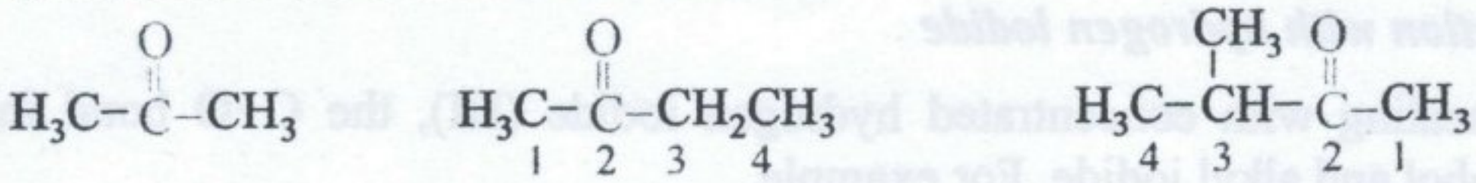
The systematic (IUPAC) names are derived from the names of the parent hydrocarbons. The suffix –al instead of –e is added to the characteristic stem. The chain is numbered, starting at the end nearest to the carbonyl group.



***Common name*:**	formaldehyde	acetaldehyde	propionaldehyde	α-methylpropionaldehyde
***IUPAC name*:**	methanal	ethanal	propanal	2-methylpropanal

The common name of a ketone consists of the names of the groups attached to the carbonyl group followed by the term ketone. The simplest ketone is called acetone.

The systematic (IUPAC) names are derived from their parent hydrocarbons. The suffix –one instead of –e is added to the characteristic stem.



***Common name*:**	acetone	ethyl methyl ketone	methyl *iso*-propyl ketone
***IUPAC name*:**	propanone	2-butanone	3-methyl-2-butanone

(ii) Methods of preparation

Oxidation of alcohols

In this method, alcohols are gently heated with an oxidising agent, i.e., acidified potassium dichromate solution. **Primary** and **secondary alcohols** give aldehydes and ketones, respectively.

The general equation for making an aldehyde is

$$\text{primary alcohol} + [O] \xrightarrow{\text{oxidising agent}} \text{aldehyde} + \text{water}$$

[O] represents nascent oxygen (oxygen atom) produced from the oxidising agent. To make the aldehyde, the primary alcohol is heated gently with acidified potassium dichromate solution.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + [O] \xrightarrow[\Delta]{K_2Cr_2O_7,\ H^+} \underset{\text{ethanal}}{CH_3CHO} + H_2O$$

Note: The aldehyde product is obtained by distillation to remove it immediately from the reaction mixture. This can be done because the aldehyde will always have a lower boiling point than its corresponding alcohol. If the aldehyde is not distilled off as soon as it is formed, further heating with the acidified dichromate solution will oxidise the aldehyde produced to a carboxylic acid.

The general equation for making a ketone is

$$\text{secondary alcohol} + [O] \xrightarrow{\text{oxidising agent}} \text{ketone} + \text{water}$$

To produce a ketone, secondary alcohol must be heated with this oxidising agent. The ketone formed cannot be further oxidised, even if the reaction mixture is refluxed and an excess oxidising agent is added. Therefore, the ketone product is not needed to be distilled off immediately.

$$\underset{\text{2-propanol}}{CH_3CHOHCH_3} + [O] \xrightarrow[\Delta]{K_2Cr_2O_7,\ H^+} \underset{\text{propanone}}{CH_3COCH_3} + H_2O$$

Hydration of alkynes

The addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ produces ethanal, whereas other alkynes produce ketones in this reaction.

$$\underset{\text{ethyne}}{HC{\equiv}CH} + H_2O \xrightarrow[HgSO_4]{\text{dil } H_2SO_4,\ 60\ ^\circ C} \underset{\text{ethanal}}{CH_3CHO}$$

$$\underset{\text{propyne}}{CH_3C{\equiv}CH} + H_2O \xrightarrow[HgSO_4]{\text{dil } H_2SO_4,\ 60\ ^\circ C} \underset{\text{propanone}}{CH_3COCH_3}$$

(iii) Properties and uses

At room temperature, methanal is a gas and ethanal is a volatile liquid. Other aldehydes and ketones are liquid or solid. Methanal, ethanal, and propanone are water soluble, however their solubility decreases as the chain length increases.

Oxidation

Aldehydes and ketones differ in their oxidation reactions.

Aldehydes are easily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate, potassium dichromate, nitric acid, etc.

$$\underset{\text{aldehyde}}{RCHO} + [O] \xrightarrow{\text{oxidising agent}} \underset{\text{carboxylic acid}}{RCOOH}$$

Ketones are generally oxidised under vigorous conditions, such as with strong oxidising agents and at high temperatures.

Reduction

Aldehydes and ketones are easily reduced to the corresponding primary and secondary alcohols, using the reducing agent lithium aluminium hydride, $LiAlH_4$, in dry ether at room temperature.

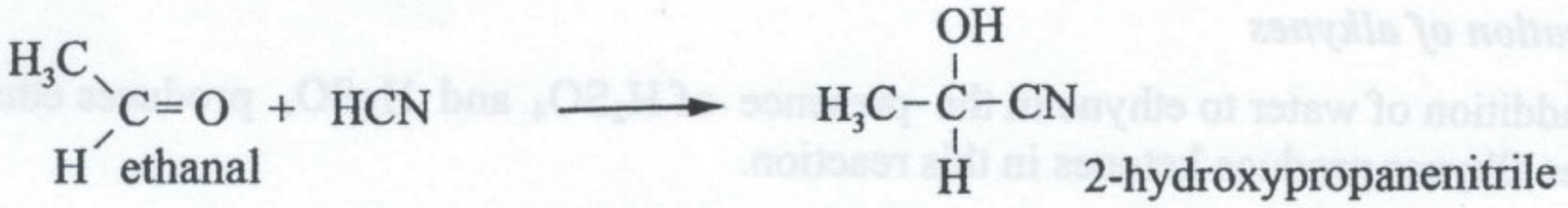
[H] represents hydrogen from the reducing agent. Dry ether is used because $LiAlH_4$ reacts violently with water. At the end of the reaction, the product is a complex aluminium salt. This is converted to alcohol by treatment with dilute sulphuric acid.

$$\underset{\text{ethanal}}{CH_3CHO} + 2[H] \xrightarrow[\text{dil } H_2SO_4]{LiAlH_4 \text{ in dry ether}} \underset{\text{ethanol}}{CH_3CH_2OH}$$

$$\underset{\text{propanone}}{CH_3COCH_3} + 2[H] \xrightarrow[\text{dil } H_2SO_4]{LiAlH_4 \text{ in dry ether}} \underset{\text{2-propanol}}{CH_3CHOHCH_3}$$

Addition with HCN

Hydrogen cyanide, HCN, adds across the carbon-oxygen double bond in aldehydes and some ketones to produce compounds known as hydroxynitriles. The HCN is generated in the reaction vessel by the reaction of sodium cyanide, NaCN, and dilute sulphuric acid.
Note: Nitriles are the organic compounds also known as cyano compounds. Inorganic compounds with -CN group are called cyanides.



Uses of aldehydes and ketones

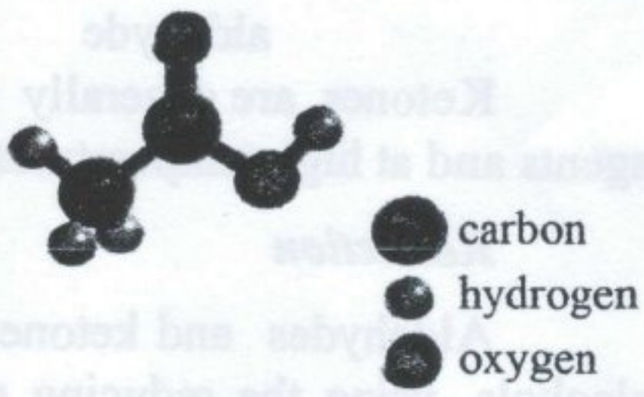
Aldehydes are versatile compounds that can help make resins, dyes and organic acids, as well as perfumes, detergents and soaps. Formalin (40 % aqueous solution of methanal) is used as a disinfectant and a preservative for biological specimens. Cinnamic aldehyde is used in some perfumes of natural, sweet, or fruity scents.

Starfish in formalin

Ketones are popular solvents for other moderately polar substances, including waxes, plastics, paints, lacquers, varnishes, and glues. The simple ketone, propanone (acetone), is used as an effective solvent in many nail polish removers, plastic cements, resins and varnishes.

(c) Carboxylic Acids

Carboxylic acids are organic compounds with a carboxyl functional group -COOH. The carboxyl group is made up of a carbonyl group and a hydroxyl group. They form a homologous series with the general formula $C_nH_{2n}O_2$. The ball-and-stick model of ethanoic acid, CH_3COOH, is shown in the illustration.



(i) Nomenclature

Several carboxylic acids have common names. Many carboxylic acid members get their common names from the Latin names of their natural sources. Formic acid was obtained by distillation of ants (Latin formica, meaning "ant") and acetic acid occurs in vinegar (Latin acetum, "vinegar").

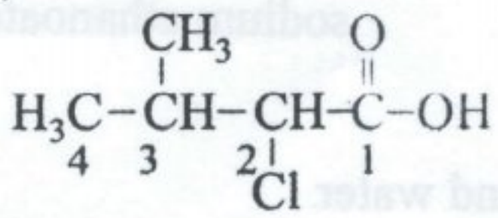
For example, HCOOH formic acid
CH_3COOH acetic acid

The IUPAC system: The -e from the name of the parent chain is replaced by -oic acid

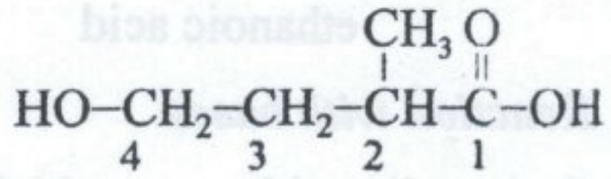
For example, HCOOH methan oic acid
CH_3COOH ethan oic acid

Since a carboxylic acid group must always be found at the end of a carbon chain, it is always given the "1" location position in numbering. If a particular compound contains more than one functional group, the nomenclature is based on the carboxyl group instead of other functional groups.

For example,



2-chloro-3-methylbutanoic acid



4-hydroxy-2-methylbutanoic acid

(ii) Methods of preparation

The general equation for the reaction in which a carboxylic acid is made from primary alcohol is

$$\text{primary alcohol} + [O] \xrightarrow[\text{reflux}]{\text{oxidising agent}} \text{carboxylic acid} + \text{water}$$

Ethanoic acid is formed by the oxidation of ethanol. There are two ways to produce ethanoic acid.

Oxidation by acidified potassium dichromate

Ethanol is oxidised by warming it with the powerful oxidising agent which is acidified potassium dichromate, using a reflux condenser.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + 2[O] \xrightarrow[\Delta]{K_2Cr_2O_7,\ H^+} \underset{\text{ethanoic acid}}{CH_3COOH} + H_2O$$

Note: Instead of a distillation set, a reflux condenser has to be used so that the volatile components remain in the reaction for long enough to complete their reaction. In this case, it is used to oxidise primary alcohol to completion, to the carboxylic acid.

Oxidation by atmospheric oxygen

Ethanol is oxidised by atmospheric oxygen in the presence of bacteria (Acetobacter).

$$\underset{\text{ethanol}}{CH_3CH_2OH} + O_2 \xrightarrow{\text{bacteria}} \underset{\text{ethanoic acid}}{CH_3COOH} + H_2O$$

(iii) Properties and uses

At room temperature, carboxylic acids which contain up to nine carbon atoms are colourless liquids with an unpleasant smell. The carboxylic acids with up to four carbons are soluble in water. Solubility decreases with the larger hydrocarbon portion. There are strong intermolecular hydrogen bonds between carboxylic acid molecules. As a result, when compared to other compounds of comparable molecular mass, they have high boiling points.

Reaction with metal

Carboxylic acids are weak acids, and they can react with reactive metals such as sodium, potassium, and magnesium to give salt and hydrogen.

$$\underset{\text{ethanoic acid}}{2CH_3COOH} + Mg \longrightarrow \underset{\text{magnesium ethanoate}}{(CH_3COO)_2Mg} + H_2$$

Reaction with metal carbonate

Carboxylic acids react with carbonates to give salt, water and carbon dioxide.

$$\underset{\text{ethanoic acid}}{2CH_3COOH} + Na_2CO_3 \longrightarrow \underset{\text{sodium ethanoate}}{2CH_3COONa} + CO_2 + H_2O$$

Reaction with bases

Carboxylic acids react with bases to give salt and water.

$$\underset{\text{ethanoic acid}}{CH_3COOH} + NaOH \longrightarrow \underset{\text{sodium ethanoate}}{CH_3COONa} + H_2O$$

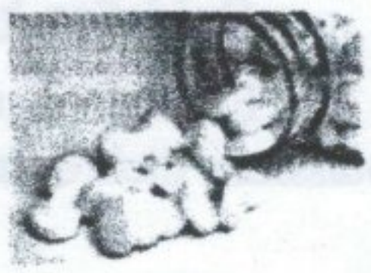
Reduction

Carboxylic acids are reduced to their corresponding primary alcohols using the reducing agent, $LiAlH_4$, in dry ether at room temperature.

$$\underset{\text{propanoic acid}}{CH_3CH_2COOH} + 4[H] \xrightarrow[\text{dil } H_2SO_4]{LiAlH_4 \text{ in dry ether}} \underset{\text{1-propanol}}{CH_3CH_2CH_2OH} + H_2O$$

Uses of carboxylic acids

Carboxylic acids are used in the production of polymers, pharmaceuticals, and food additives. Carboxylic acids are used in the manufacture of drugs like antibiotics, antihistamines and so on. The popular painkiller, aspirin, is the acetyl derivative of salicylic acid. Carboxylic acids are used in many industries. For instance, methanoic acid is used in the textiles, rubber, and leather industries. Ethanoic acid and sodium benzoate (sodium salt of benzoic acid) are used in the food industry.



Aspirin

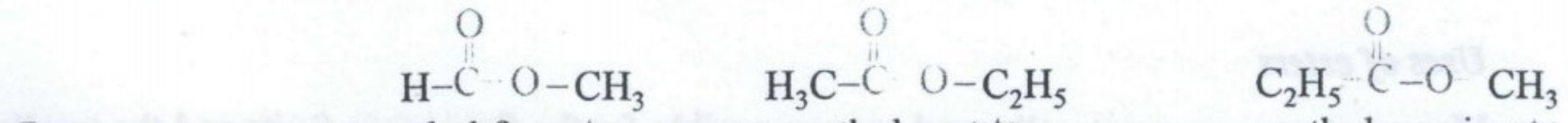
(d) Esters

Esters are carboxylic acid derivatives in which the hydroxyl (-OH) group has been replaced by an alkoxy (-OR) group, producing the following arrangement.

The ball-and-stick model of methyl ethanoate, CH_3COOCH_3, is shown in the illustration.

(i) Nomenclature

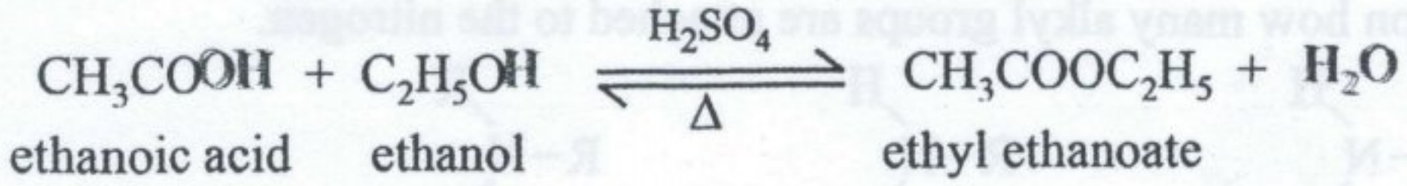
The general ester, RCOOR' can be derived from the carboxylic acid RCOOH and the alcohol R'OH. The name of an ester is formed by writing the name of the alkyl group followed by the name of the acid with the -ic acid ending replaced by -ate. Examples are given below.



***Common name*:**	methyl formate	ethyl acetate	methyl propionate
***IUPAC name*:**	methyl methanoate	ethyl ethanoate	methyl propanoate

(ii) Methods of preparation

Generally, carboxylic acid can react with alcohol to form ester in a process which is known as **esterification**. When ethanoic acid is warmed with ethanol in the presence of a few drops of concentrated sulphuric acid, water and ethyl ethanoate (an ester) are formed.



$$CH_3COOH + C_2H_5OH \underset{\Delta}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$

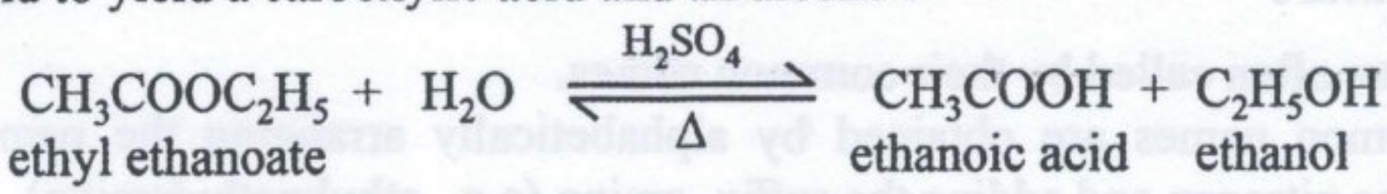
ethanoic acid ethanol ethyl ethanoate

(iii) Properties and uses

Carboxylic acid esters of low molecular mass are colourless, volatile liquids with pleasant odours. They are slightly soluble in water. The solubility of esters in water decreases rapidly with an increase in molecular mass. The boiling points of esters are lower than those of the corresponding parent acids.

Acidic hydrolysis

Acidic hydrolysis is simply the reverse of esterification. An ester is hydrolysed by using an aqueous acid to yield a carboxylic acid and an alcohol.

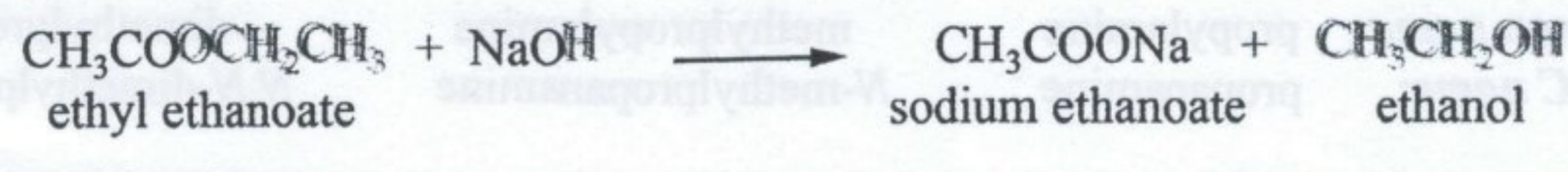


$$CH_3COOC_2H_5 + H_2O \underset{\Delta}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3COOH + C_2H_5OH$$

ethyl ethanoate ethanoic acid ethanol

Basic hydrolysis

When an ester is refluxed with an alkali (a soluble base), such as aqueous sodium hydroxide, it is fully hydrolysed. Unlike acid hydrolysis, this is not a reversible reaction, so all the ester present can be broken down by excess alkali. An alcohol and the sodium salt of the carboxylic acid are formed.

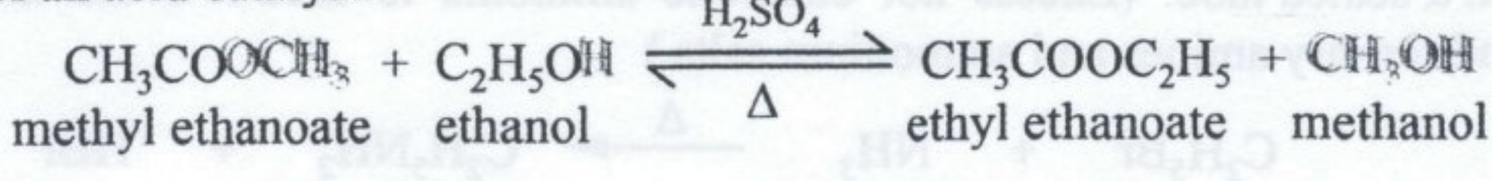


$$CH_3COOCH_2CH_3 + NaOH \longrightarrow CH_3COONa + CH_3CH_2OH$$

ethyl ethanoate sodium ethanoate ethanol

Transesterification

The most common method of transesterification is the reaction of the ester with an alcohol in the presence of an acid catalyst.



$$CH_3COOCH_3 + C_2H_5OH \underset{\Delta}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3COOC_2H_5 + CH_3OH$$

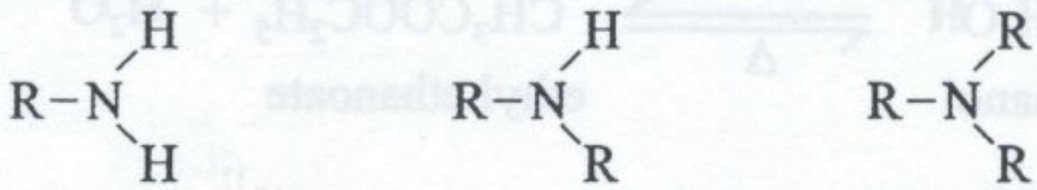
methyl ethanoate ethanol ethyl ethanoate methanol

Uses of esters

Many esters occur naturally and are responsible for the flavours in fruits and the smells of flowers. Esters are used in the preparation of artificial food flavourings. Esters are used as an organic solvent for cosmetics, perfumes and glues. Naturally-occurring esters (animal fats or vegetable oil) mixed with NaOH produce soap that is used for washing dishes and clothes.

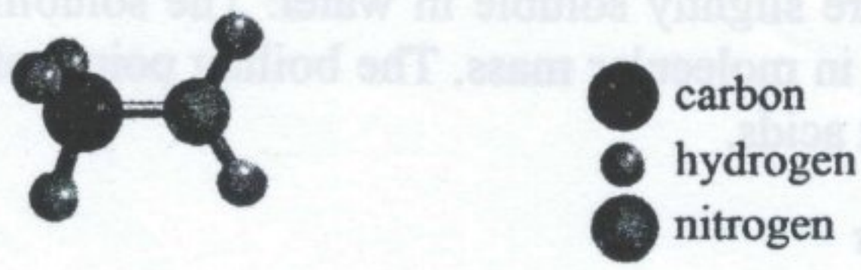
(e) Amines

An amine is a compound in which one or more hydrogen atoms of ammonia have been replaced by alkyl groups. Amines are classified as primary (1°), secondary (2°), and tertiary (3°), depending on how many alkyl groups are attached to the nitrogen.



1° amine 2° amine 3° amine

The ball-and-stick model for the simplest amine, methylamine (CH_3NH_2) is shown in the diagram.

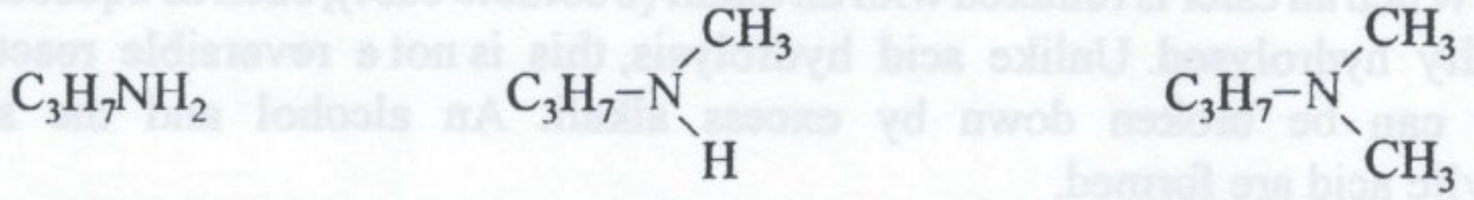


(i) Nomenclature

Amines are often called by their common names.

The common names are obtained by alphabetically arranging the names of the alkyl substituents on the nitrogen and adding the suffix -amine (e.g., ethylmethylamine).

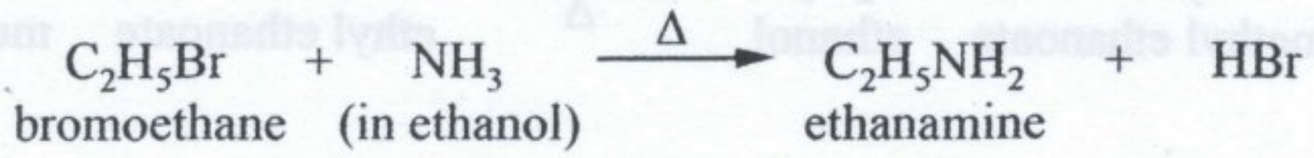
In the IUPAC system, the -e from the name of the parent chain is replaced by -amine. The presence of alkyl substituents attached to nitrogen is designated by prefixing the letter *N*.



Common name:	propylamine	methylpropylamine	dimethylpropylamine
IUPAC name:	propanamine	*N*-methylpropanamine	*N,N*-dimethylpropanamine

(ii) Methods of preparation

Ethanamine is prepared by heating bromoethane with an excess of ammonia dissolved in ethanol in a sealed tube. (Excess hot ethanolic ammonia is used to avoid the formation of secondary and tertiary amines and ammonium salts.)



bromoethane (in ethanol) ethanamine

Bromoethane (ethyl bromide) can be prepared from the reaction between ethanol and hydrogen bromide in the presence of a small amount of sulphuric acid.

$$\underset{\text{ethanol}}{C_2H_5OH} + HBr \xrightarrow{H_2SO_4} \underset{\text{bromoethane}}{C_2H_5Br} + H_2O$$

(iii) Properties and uses

Methyl, dimethyl, trimethyl, and ethyl amines are gases under standard conditions. Most common alkyl amines are liquids, and high molecular mass amines are solids. The smell of gaseous amines is similar to that of ammonia, while liquid amines possess a fishy smell. Because more hydrogen bonds are formed in primary amines, they are more soluble in water than secondary and tertiary amines.

Primary and secondary amines have higher boiling points than those of alkanes or ethers of a similar molecular mass because they can form an intermolecular hydrogen bonding. However, their boiling points are lower than those of alcohols which have the same number of carbon atoms. Alcohol molecules have hydrogen atoms bonded to a more electronegative oxygen atom.

Carbylamine reaction

Ethanamine (ethylamine) reacts with chloroform in the presence of an alkali to form ethyl isocyanide (ethyl carbylamine) with an unpleasant smell. This reaction is known as carbylamine reaction used to identify the primary amines.

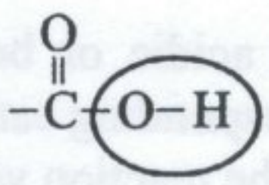
$$\underset{\text{ethanamine}}{CH_3CH_2NH_2} + CHCl_3 + \underset{\text{(in alcohol)}}{3KOH} \longrightarrow \underset{\text{ethyl isocyanide}}{CH_3CH_2NC} + 3KCl + 3H_2O$$

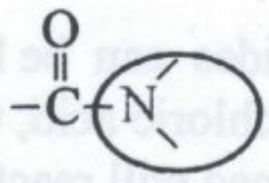
Uses of amines

Amines are used in making azo-dyes and nylon apart from medicines and drugs. They are widely used in developing chemicals for crop protection, medication and water purification.

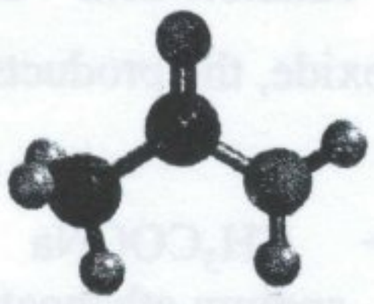
(f) Amides

Amides are carboxylic acid derivatives in which the –OH of the carboxylic acid has been replaced by $–NH_2$, –NHR, or $–NR_2$ of an amine, producing the following arrangement.





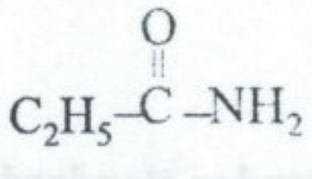
The ball-and-stick model of ethanamide, CH_3CONH_2, is shown in the illustration.

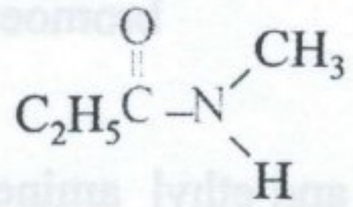


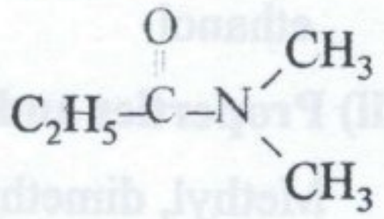
carbon
hydrogen
nitrogen
oxygen

(i) Nomenclature

Amides are named as derivatives of the corresponding carboxylic acids, the suffix -amide being substituted for –oic acid in the name of the parent acid. The presence of alkyl substituents attached to nitrogen is designated by prefixing the letter *N*.





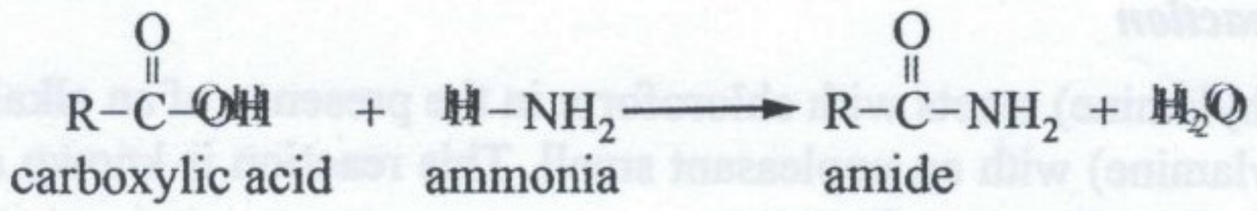


***Common name*:**	propionamide	*N*-methylpropionamide	*N,N*-dimethylpropionamide
***IUPAC name*:**	propanamide	*N*-methylpropanamide	*N,N*-dimethylpropanamide

(ii) Methods of preparation

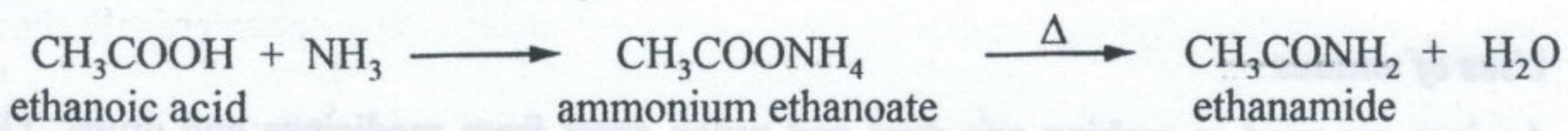
Condensation reaction

The addition of ammonia (NH_3) to a carboxylic acid forms an amide. The reaction is a **condensation reaction** as a small molecule, in this case water, is eliminated when the reactant molecules join together.



carboxylic acid ammonia amide

The excess ethanoic acid is first converted into an ammonium salt which then produces ethanamide on heating. The excess ethanoic acid is there to prevent dissociation of the ammonium salt before it dehydrates.



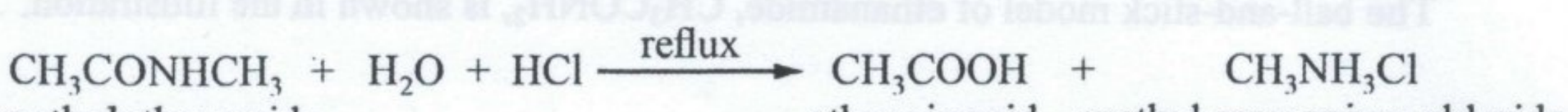
ethanoic acid ammonium ethanoate ethanamide

(iii) Properties and uses

Methanamide is a liquid while all simple amides are solids. Amides containing five or fewer carbon atoms are water soluble. Like esters, aqueous solutions of amides are usually neutral. Generally, the amides have high boiling points and melting points.

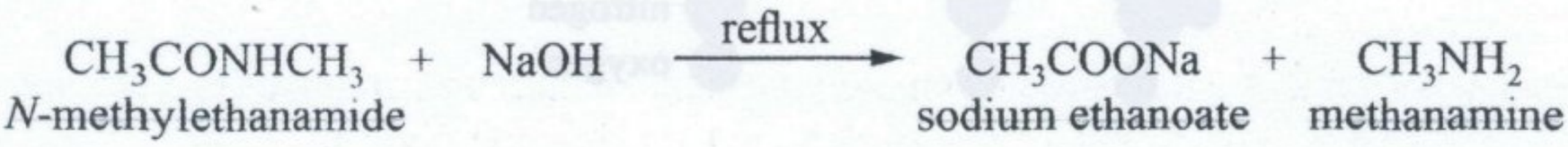
Hydrolysis

Generally, amides can be hydrolysed in either acidic or basic solutions. If the amide is refluxed with hydrochloric acid, the products are corresponding carboxylic acid and a primary amine. The amine formed will react with excess acid in the reaction vessel to make its ammonium salt.



N-methylethanamide ethanoic acid methyl ammonium chloride

With an alkali, such as aqueous sodium hydroxide, the products are the sodium salt of the carboxylic acid and the primary amine.



N-methylethanamide sodium ethanoate methanamine

Uses of amides

Amides are widely used in industries in producing plastic, rubber, paper, colour in crayons, pencils and ink as well as used in water and sewage treatments. Amides such as nylon are used in textiles, to produce ropes, bulletproof vests and tyre cords.

REVIEW QUESTIONS

(1) Name the given compounds according to the IUPAC system.
$CH_3COCH_2CH_3$, $(CH_3)_3CCH_2COOH$, CH_3COOCH_3, $CH_3CH_2CONH_2$

(2) Identify unknown substances **Q, R, S** and **T** in the following reactions:
(a) **Q** + magnesium ⟶ magnesium methanoate + **R** (gas)
(b) **S** + sodium hydroxide ⟶ sodium ethanoate + water
(c) ethanoic acid + **T** $\underset{\Delta}{\overset{H_2SO_4}{\rightleftharpoons}}$ methyl ethanoate + water

(3) Write the formulae of the reactants needed to prepare each of the following esters:
(a) $CH_3COOCH_2CH_2CH_3$ (smells like pears)
(b) $CH_3COOCH_2CH_2CH_2CH_2CH_3$ (smells like bananas)

Key Terms

- **Primary alcohol** is an alcohol with a $-CH_3$ or $R-CH_2-$ group bonded to the -OH group.
- **Secondary alcohol** is an alcohol with two R- groups bonded to the carbon bearing the -OH group.
- **Esterification** is the reaction of an alcohol with an acid to produce an ester and water.
- **Transesterification** is the reaction of an ester with an alcohol to form a different ester.
- **Condensation reaction** is the reaction in which a small molecule, such as water is eliminated when two molecules are joined.

8.2 DETERMINING THE FUNCTIONAL GROUPS IN ORGANIC COMPOUNDS

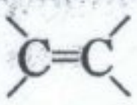
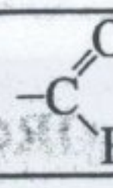
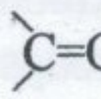
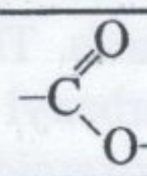
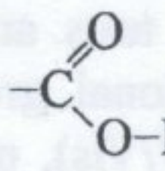
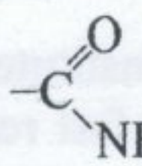
As mentioned in Section 8.1 of the Grade 11 Chemistry Textbook, an alkane lacks functional groups whereas an alkene and an alkyne have functional groups which are carbon-carbon double bond and carbon-carbon triple bond, respectively. The groups of atoms that are attached to the carbon backbone of organic compounds are known as functional groups, which are responsible for the characteristic chemical reactions of organic compounds. The most common functional groups in organic compounds other than hydrocarbons are carbonyl (C=O), hydroxyl (OH), carboxyl (COOH), carboalkoxy (COOR), amine (NH_2) and carboxamide ($CONH_2$). The identification of the organic compound is based on simple chemical tests and spectroscopic techniques that indicate the presence (or absence) of specific functional groups. The most important common techniques are infrared (IR), ultraviolet/visible (UV/Vis), nuclear magnetic resonance (NMR), and mass spectrometry (MS). In this section, infrared (IR) spectroscopy will only be described.

(a) Chemical Tests

The analysis and identification of unknown organic compound constitute a very important aspect of experimental organic chemistry. A chemical test is typically a fast reaction performed

in a test tube that gives a visual clue (a colour change, precipitate, or gas formation) as evidence for a chemical reaction. The functional group in an organic compound can undergo a structural change in a reaction and also affect the solubility of the compound in water or organic solvents. A specific functional group in a molecule can be identified using certain chemical tests. Table 8.1 shows some chemical tests to identify functional groups of organic compounds - hydrocarbons, alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, amines and amides.

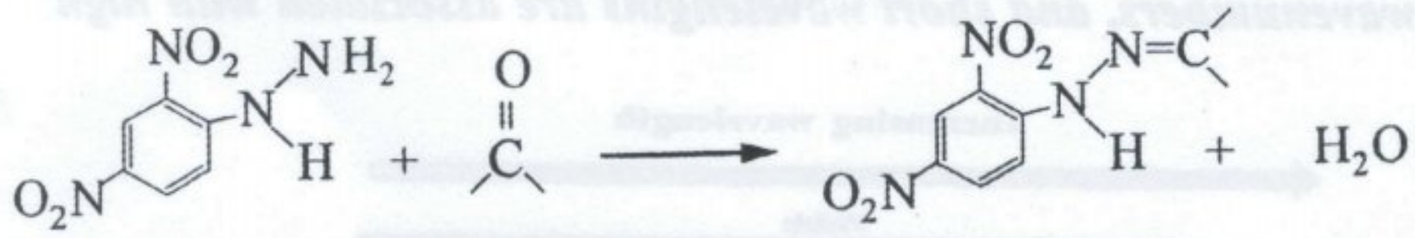
Table 8.1 Chemical Tests for Some Organic Compounds

Family	Functional Group	Example of Compound	Chemical Test	Observation
alkanes	-	$H_3C–CH_3$	Mix with 1% $KMnO_4$ solution.	no decolourisation
alkenes		$H_2C=CH_2$	Mix with 1% $KMnO_4$ solution.	decolourisation
alkynes	–C≡C–	HC≡CH	Pass through ammoniacal Cu_2Cl_2 solution.	red coloured precipitate
alcohols	–O–H	CH_3CH_2OH	Warm with acidified $K_2Cr_2O_7$ solution.	orange colour of solution changes to green colour
ethers	R–O–R'	CH_3OCH_3	Boil with HI and then react with $AgNO_3$.	yellow coloured precipitate
aldehydes		HCHO	Heat gently with Fehling's solution.	reddish-brown coloured precipitate
ketones		CH_3COCH_3	Mix with 2,4 dinitrophenylhydrazine (2,4-DNP) solution.	deep-orange coloured precipitate
			Heat gently with Fehling's solution.	no precipitate
carboxylic acids		CH_3COOH	Mix with saturated $NaHCO_3$ solution.	evolution of CO_2 (test with limewater)
esters		CH_3COOCH_3	Heat gently with EtOH, phenolphthalein and dil NaOH.(pink)	decolourisation
primary amines	$–NH_2$	CH_3NH_2	React with $CHCl_3$ in the presence of alkali.	unpleasant smell
primary amides		CH_3CONH_2	Boil with 20 % NaOH solution.	evolution of NH_3 (test with HCl)

2,4-DNP Test

The presence of a carbonyl group such as aldehyde or ketone can be easily tested by using a solution of 2,4-DNP (2,4-dinitrophenylhydrazine). If an aldehyde or ketone is present, a deep-orange precipitate is formed.

The orange precipitate formed from 2,4 DNP Test

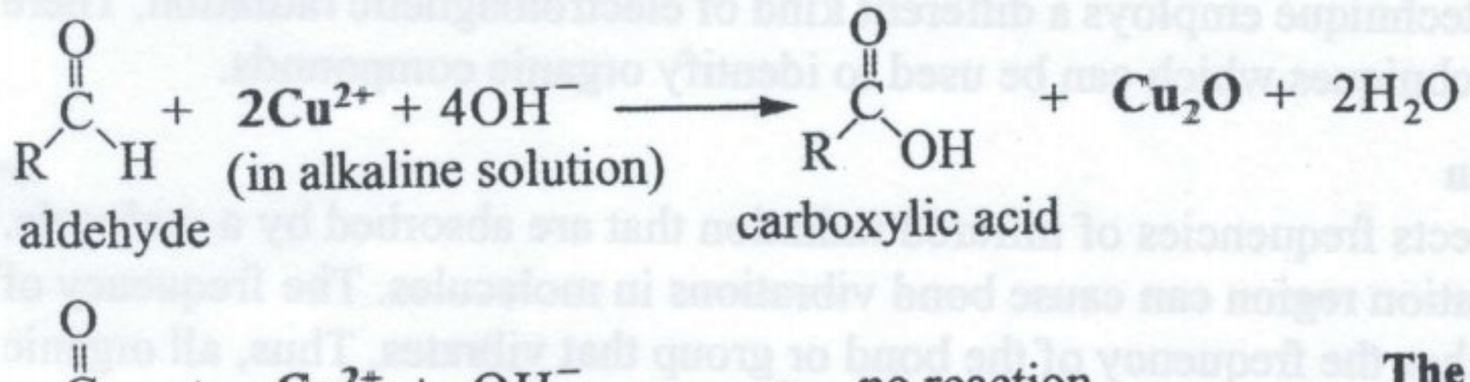


2,4-dinitrophenylhydrazine 2,4-dinitrophenylhydrazone

Fehling's Test

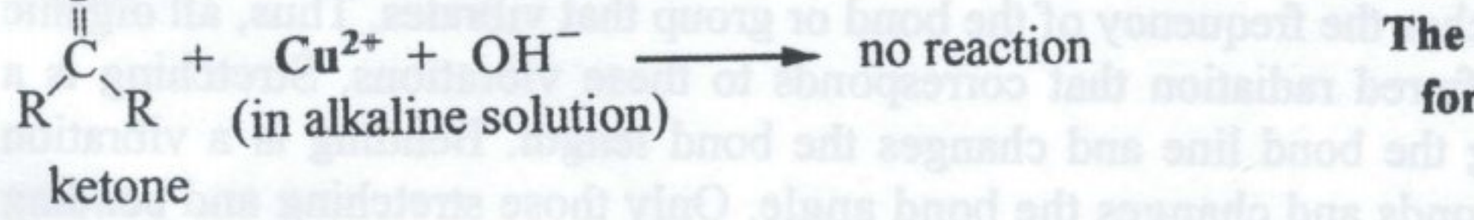
Fehling's solution can be used to distinguish aldehyde and ketone functional groups. As described in Section 8.1 (b), aldehydes can be further oxidised to form carboxylic acids, but ketones cannot be oxidised easily. This difference can be used to distinguish between an aldehyde and a ketone in a simple chemical test.

Fehling's solution is an alkaline solution containing copper(II) ions. When the clear blue Fehling's solution is warmed with an aldehyde, the reddish-brown precipitate is formed. However, a ketone does not give precipitate with Fehling's solution.



aldehyde carboxylic acid

The reddish-brown precipitate formed from Fehling's Test



ketone

Chemical tests are handy but not always practical for the identification of compounds with complex structures.

(b) Infrared Spectroscopy

The spectroscopic techniques can be performed quickly on small amounts of a compound and can provide much more information about the compound's structure. Additionally, they are also non-destructive techniques compared to methods using chemical reactions. Infrared (IR) spectroscopy is the study of the absorption of light by a compound, in the infrared region of electromagnetic spectrum. Hence, one should understand the interaction of matter and **electromagnetic radiation**.

(i) Electromagnetic radiation

A continuum of different types of electromagnetic radiation, each associated with a particular energy range, makes up the electromagnetic spectrum (Figure 8.1). Because electromagnetic radiation has wave-like properties, it is characterised by either its **frequency** or its **wavelength**. The relationship between the energy (E) and the frequency

(ν) or wavelength (λ) of the electromagnetic radiation is described by Planck's equation, $E = h\nu = \frac{hc}{\lambda}$, where h is Planck's constant and c is the speed of light. **Wavenumber** (measured in cm^{-1}) which is the reciprocal of the wavelength, is one way to describe the frequency of electromagnetic radiation, and it is the one most commonly used in **infrared spectroscopy**.

High frequencies, large wavenumbers, and short wavelengths are associated with high energies.

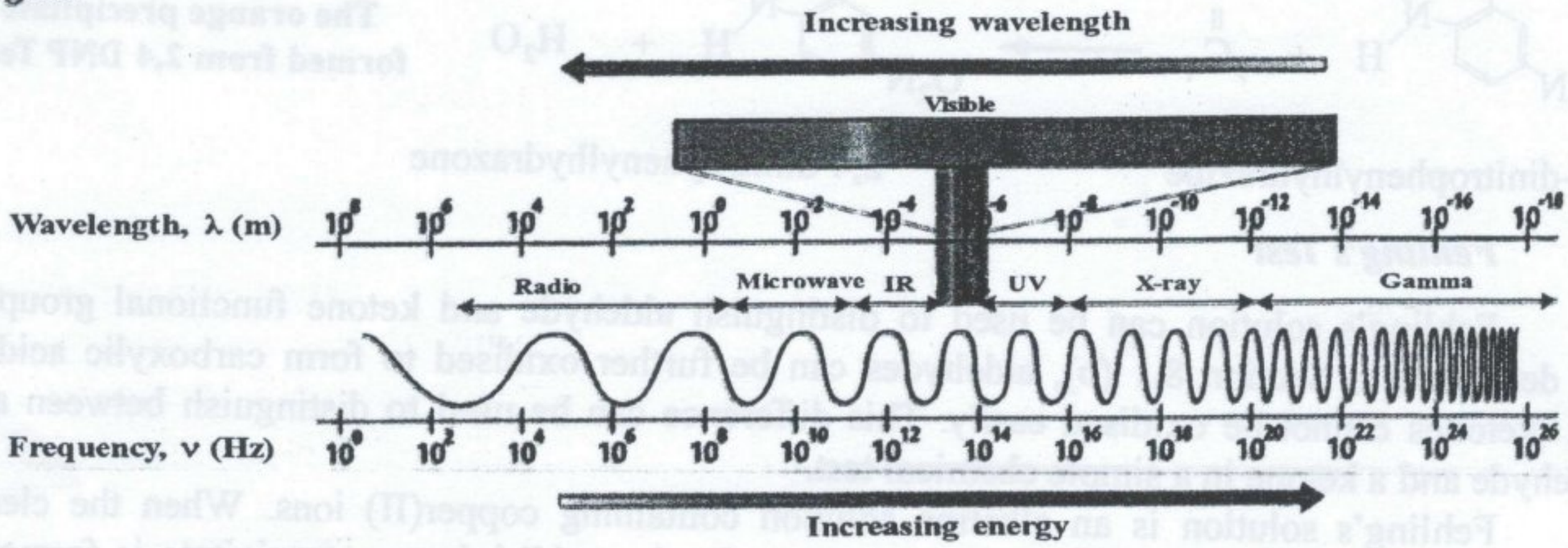


Figure 8.1 The Electromagnetic Spectrum

Each spectroscopic technique employs a different kind of electromagnetic radiation. There are several spectroscopic techniques which can be used to identify organic compounds.

(ii) Molecular vibration

IR spectroscopy detects frequencies of infrared radiation that are absorbed by a molecule. Photons in the infrared radiation region can cause bond vibrations in molecules. The frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. Thus, all organic compounds will absorb infrared radiation that corresponds to these vibrations. Stretching is a vibration that occurs along the bond line and changes the bond length. Bending is a vibration that occurs between two bonds and changes the bond angle. Only those stretching and bending motions that change the dipole moment of a molecule give rise to the absorption of infrared radiation. Hence, homonuclear diatomic molecules (e.g., N_2) which have no dipole moments are IR inactive. On the other hand, heteronuclear diatomic molecules (e.g., CO) which have dipole moments are IR active.

Each stretching and bending vibration occurs with a characteristic frequency which depends on the bond strength and the masses of the atoms. Light atoms, for example, vibrate at higher frequencies than heavier atoms and multiple bonds vibrate at higher frequencies than single bonds. It takes more energy to stretch a bond than to bend it.

Obtaining the IR spectrum

The instrument used to obtain an infrared spectrum is called an IR spectrometer. When a sample is irradiated with electromagnetic radiation in the infrared region, an IR spectrum is obtained. It is a plot of the percent transmittance or absorbance of radiation versus the wavenumber of the radiation transmitted. The IR spectrum of propanone is given in Figure 8.2 as an example. The stretching and bending vibrations of C=O and C-H are observed at the corresponding frequencies (in terms of wavenumbers) in this spectrum.

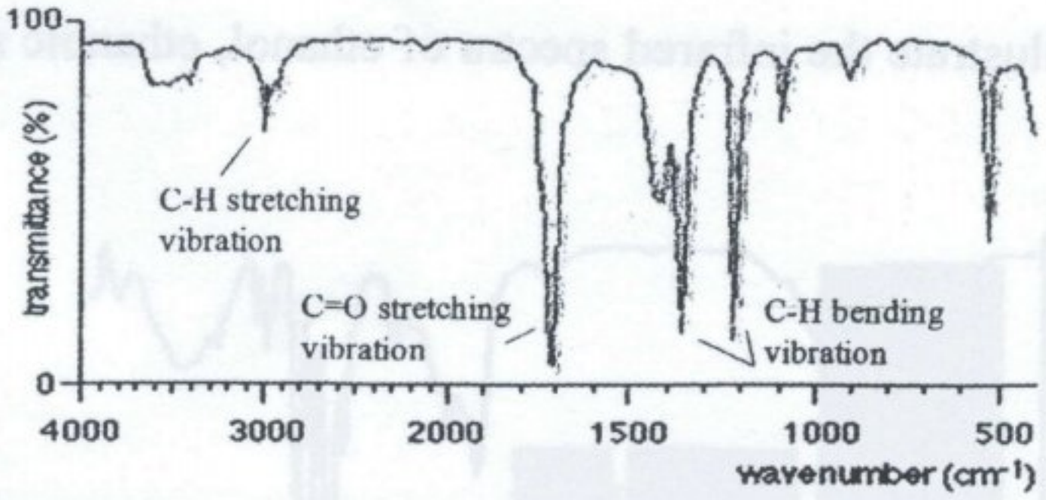


Figure 8.2 Infrared Spectrum of Propanone, CH_3COCH_3

(iii) Characteristic IR absorption bands

Different functional groups produce bond absorptions at different locations and intensities (broad or sharp, strong or weak) on the IR spectrum. Therefore, the presence or absence of different functional groups can be identified from the transmittance/absorbance pattern of an infrared spectrum. Each functional group has characteristic absorption range of wavenumbers. The wavenumber and intensity associated with the vibrations of some common bonds in organic compounds are shown in Table 8.2.

Table 8.2 Some Characteristic Infrared Absorption Bands and Their Intensities

Classes of compounds	Bond	Wavenumber (cm^{-1})	Band intensity
alcohols, ethers, esters, carboxylic acids	C-O	1050-1410	strong
alkenes, aromatic compounds	C=C	1620-1680	medium, weak
amides, ketones, aldehydes, esters, carboxylic acids	C=O	1650-1750	strong, sharp
alkynes	C≡C	2100-2260	medium, weak
carboxylic acids	O-H	2500-3300	strong, very broad
aldehydes	C-H	2720-2820	medium, weak
alkanes, alkenes	C-H	2850-3090	strong
alcohols	O-H	3200-3600	strong
amines, amides	N-H	3300-3500	strong

The important factors that influence the intensity of an absorption band are polarity of the bond and number of bonds. The higher bond polarity and more number of bonds in molecules will give a more intense absorption band.

The presence of hydrogen bonds in molecules also affects the shape of the absorption bands. The polar O–H bond usually shows strong and broad absorption bands that are easy to identify. The broad shape of the absorption band results from the hydrogen bonding of the OH groups between molecules. The OH bond of alcohols usually has an absorption in the range of 3200-3600 cm^{-1}, while the OH bond of carboxylic acids occurs in the range of 2500-3300 cm^{-1}.

Consider N–H stretches (stretching bands) in amine and amide which are medium intensity and width compared to O–H stretches. Although N–H and O–H stretches show up in the same wavenumber region, N–H stretch is narrow and weak while the O–H strech is broad and strong. This is due to the more polarity and presence of stronger hydrogen bond of O–H.

Figures 8.3, 8.4, and 8.5 illustrate the infrared spectra of ethanol, ethanoic acid and ethanamine, respectively.

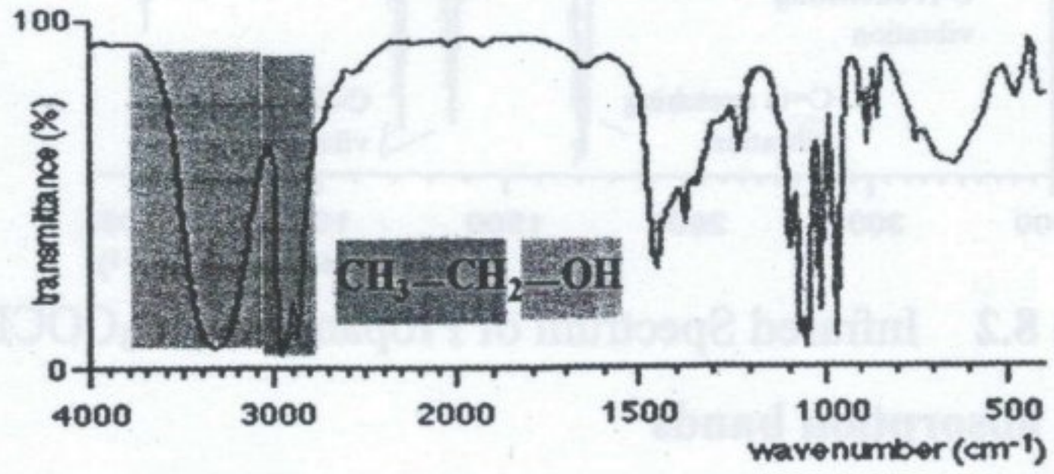


Figure 8.3 Infrared Spectrum of Ethanol, CH_3CH_2OH

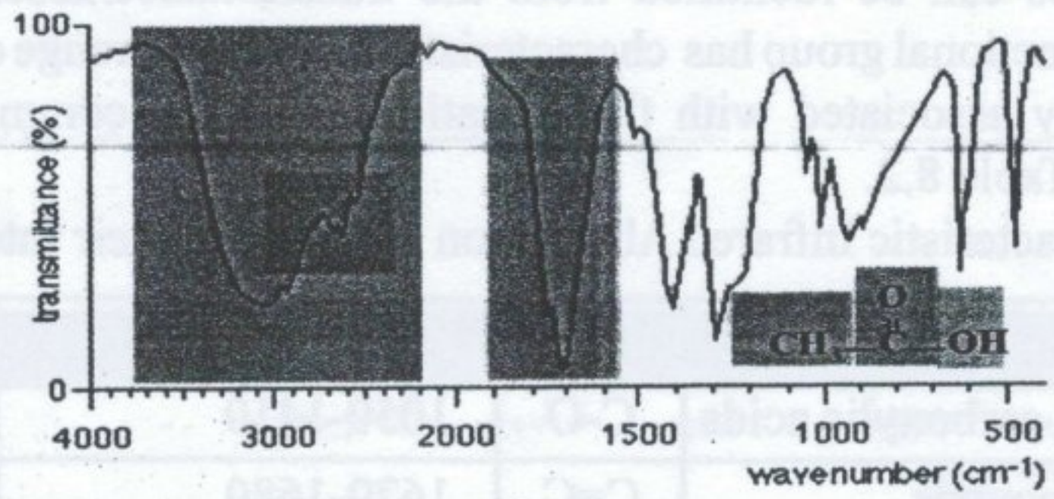


Figure 8.4 Infrared Spectrum of Ethanoic Acid, CH_3COOH

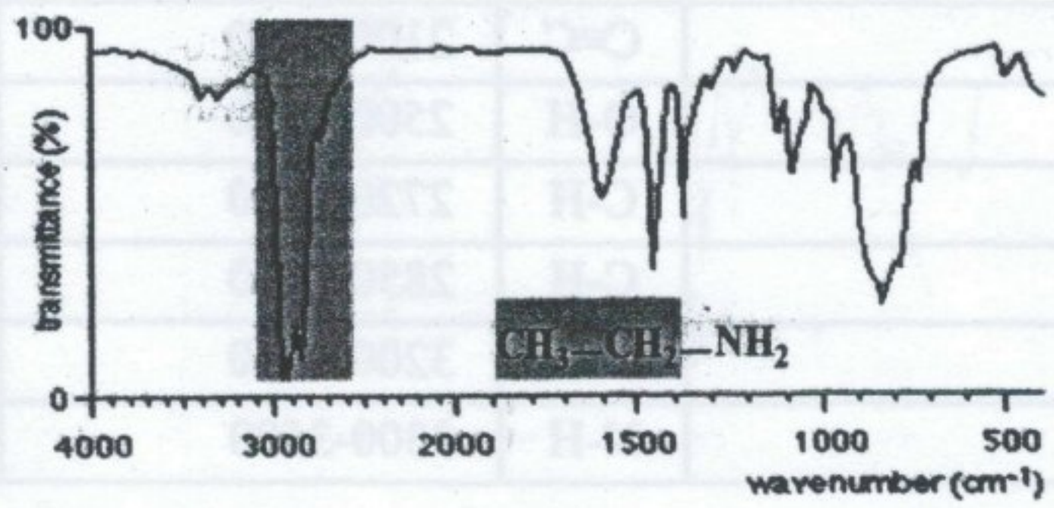


Figure 8.5 Infrared Spectrum of Ethanamine, $CH_3CH_2NH_2$

REVIEW QUESTIONS

(1) Name one reagent that is used to distinguish propanal from propanone (acetone).
(2) Which is higher in energy of the following?
   (i) electromagnetic radiation with wavenumber 100 cm^{-1} or with wavenumber 2000 cm^{-1}
   (ii) electromagnetic radiation with wavelength 950 nm or with wavelength 850 nm
(3) The infrared spectrum was obtained from a compound and showed absorptions at 1700 cm^{-1}, and 1200 cm^{-1}. Which of the following compounds could account for this spectrum?
   CH_3COOCH_3, CH_3COOH, CH_3CH_2OH

Key Terms

- **Spectroscopy** is the study of the interaction of matter and electromagnetic radiation.
- **Electromagnetic radiation** is the radiant energy that displays wave properties.
- **Frequency** is the number of wave crests that pass by a given point in one second.
- **Wavelength** is the distance from any point on one wave to the corresponding point on the next wave.
- **Wavenumber** is the number of wave crests that pass in one centimetre.
- **Infrared spectroscopy** is a technique for identifying compounds based on the change in vibrations of particular atoms when infrared radiation of specific frequencies is absorbed.

8.3 MACROMOLECULES

A macromolecule is a very large molecule that contains thousands of atoms or more, because "macro" means large. Many of the things in the environment are made up of macromolecules. Carbohydrates (starch, cellulose), proteins and natural fibres (cotton) are found in nature. The biologically important proteins and nucleic acids are made up of macromolecular units. Some of the synthetic macromolecules produced by industries are plastics, resins, nylon, and rubber.

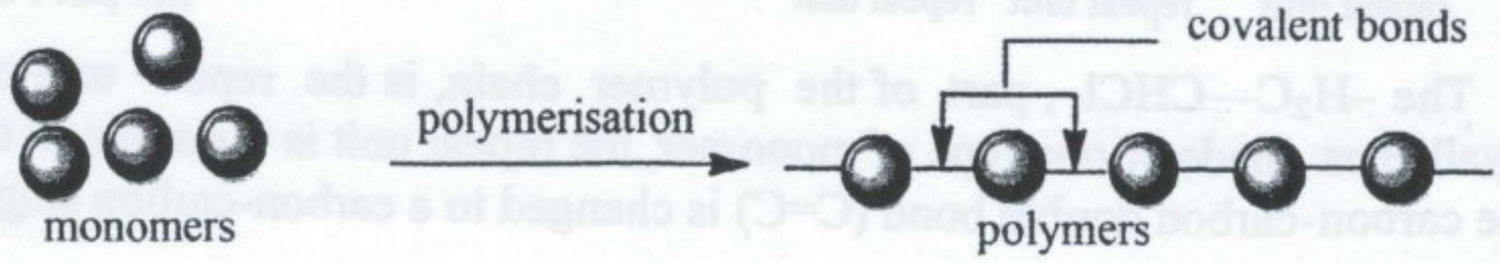
(a) Introducing Polymers

A **polymer** is a type of long-chain macromolecule that is linked together by many small repeat units known as **monomers**. If a polymer consists of only one kind of monomers then it is called a **homopolymer**, while a polymer which consists of more than one kind of monomers is called a **copolymer**. Polymers are either found in nature or produced in a laboratory. Table 8.3 shows some examples of natural and synthetic polymers.

Table 8.3 Some Examples of Natural and Synthetic Polymers

Natural polymers		Synthetic polymers	
proteins	wool	polyethene	polyvinyl chloride (PVC)
DNA	natural rubber	nylon	polyvinyl acetate (PVA)
starch	silk	terylene	polystyrene
cellulose	hair	teflon	polypropylene

When a polymer is made, monomers bond together one after another in a rapid series of steps. The process of joining together a large number of monomers to form a polymer is called **polymerisation**.



Based on the kinds of reactions involved, polymerisation is divided into two groups known as **addition polymerisation** and **condensation polymerisation**. Addition polymerisation occurs when unsaturated monomers join together without losing any molecules or atoms. Condensation

polymerisation occurs when the monomers combine to form a polymer, with the removal of a small molecule such as water.

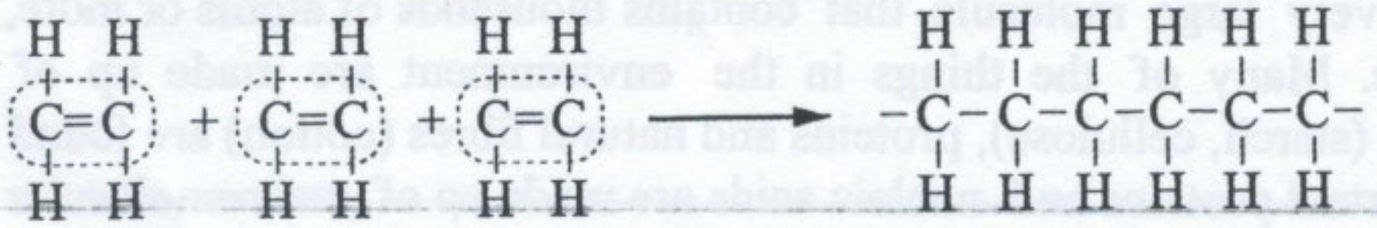
(b) Addition Polymers

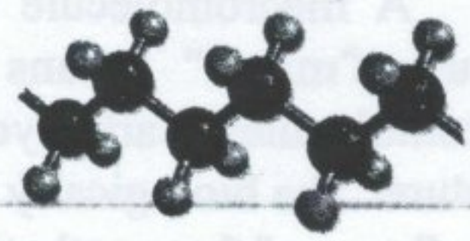
An addition polymer is a polymer formed by addition polymerisation between monomers that contain a double bond.

(i) Polyethene

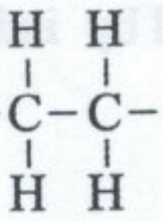
The simplest addition polymer is polyethene or polyethylene (PE). It is produced by the addition polymerisation of ethene monomers.

At high temperature and pressure, and in the presence of a catalyst, the carbon-carbon double bonds of the ethene molecules (monomers) break. Each monomer forms single bonds with two other monomers. Eventually, they join to form the polymer, polyethene.





A ball and stick model showing the part of polyethene

The repeat unit of polyethene is  .

The formula of a polymer can be written using its repeat unit (monomer). The letter "n" represents a large number. The number of ethene molecules in each polyethene molecule varies from 10,000 to 30,000.

$$n H_2C{=}CH_2 \xrightarrow[\text{catalyst}]{\text{high temperature and pressure}} \text{-}(H_2C{-}CH_2)\text{-}_n$$

ethene — polyethene

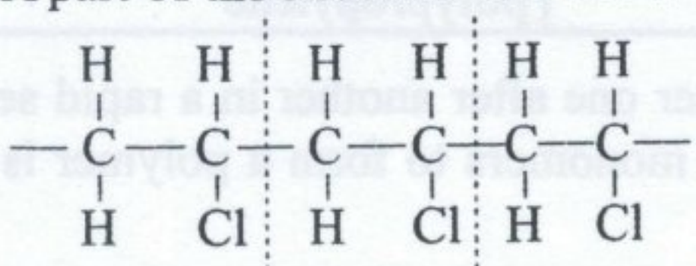
(ii) Polyvinyl chloride

Another example of an addition polymer is polychloroethene or polyvinyl chloride (PVC). The substituted alkenes, such as chloroethene (vinyl chloride), are monomer units.

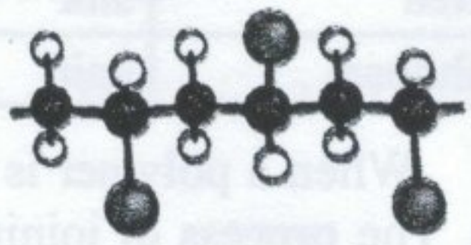
$$n H_2C{=}CHCl \xrightarrow[\text{catalyst}]{\text{high temperature and pressure}} \text{-}(H_2C{-}CHCl)\text{-}_n$$

chloroethene — polychloroethene

A part of the structure of PVC is shown below.



repeat unit repeat unit repeat unit



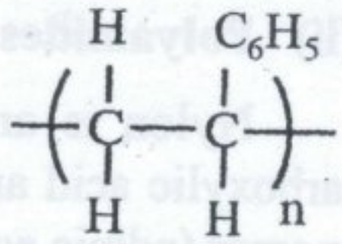
A ball and stick model showing the part of polychloroethene

The $-H_2C—CHCl-$, part of the polymer chain, is the repeat unit of polychloroethene. In polyalkenes made of one type of monomer, the repeat unit is the same as the monomer except that the carbon-carbon double bond (C=C) is changed to a carbon-carbon single bond (C–C).

(iii) Properties and uses

Addition polymers are sometimes referred to as plastics. The thermal stability of plastics depends on their types. They swell or dissolve in organic solvents and have poor weather resistance. At low temperatures, they lose plasticity and elasticity and become brittle.

Polyethene is one of the most common plastics. Polyethene can be easily moulded into various shapes. Thus, many plastic toys, bags and buckets are made of polyethene. Polyvinyl chloride's strong, lightweight and durable characteristics make it ideal for pipes, raincoats, thin gloves and flooring mats. Many frying pans are coated with a layer of teflon, $+F_2C\text{-}CF_2+_n$. Teflon is heat-resistant and has non-stick properties. Polystyrene is hard, light and brittle. Polystyrene (also known as styrofoam) is used to make disposable containers.



Polystyrene

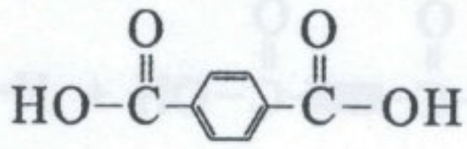
disposable containers

(c) Condensation Polymers

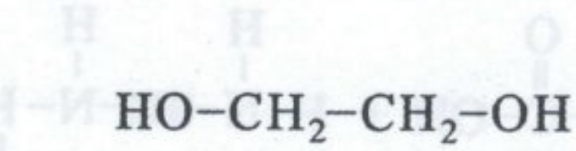
Condensation polymers are polymers whose process of polymerisation involves a condensation reaction. Condensation polymerisation is characterised by monomers that contain two different functional groups. The presence of these two different of functional groups is required within the same molecule or in two different molecules.

(i) Polyesters

Terylene is an example of condensation polymers. Terylene or polyethylene terephthalate (PET) is formed from the reaction of an acid monomer (terephthalic acid) and an alcohol monomer (ethylene glycol).

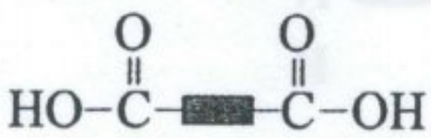


terephthalic acid
(dicarboxylic acid)

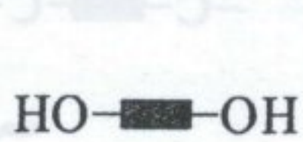


ethane- 1,2-diol (ethylene glycol)
(dialcohol)

The two monomers are represented as follows: (The blocks represent parts of the monomers.)



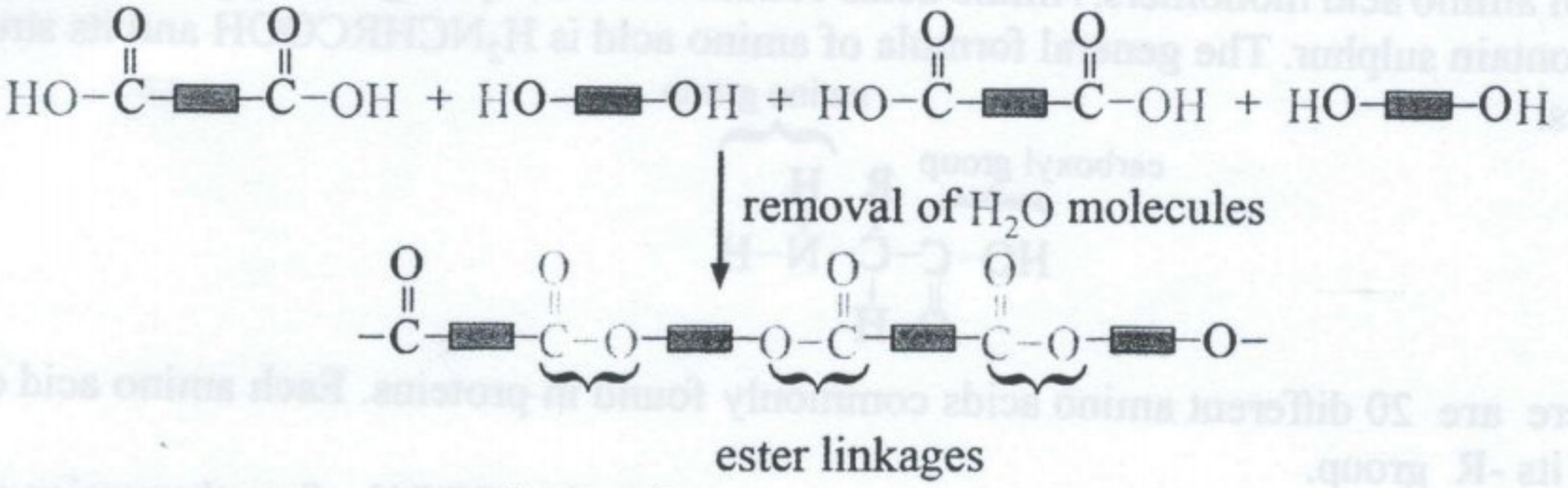
dicarboxylic acid
(an acid with two −COOH groups)



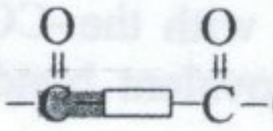
diol
(an alcohol with two −OH groups)

In the condensation polymerisation process, a hydrogen atom is lost from the alcohol, and a hydroxyl group is lost from the carboxylic acid. Together these form one water molecule which is lost during condensation reactions. The monomers are joined together by the ester linkage.

Terylene is polyester as it contains many ester linkages.

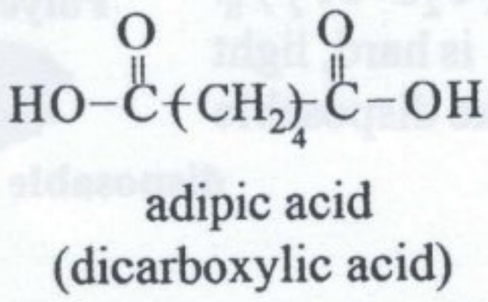


ester linkages

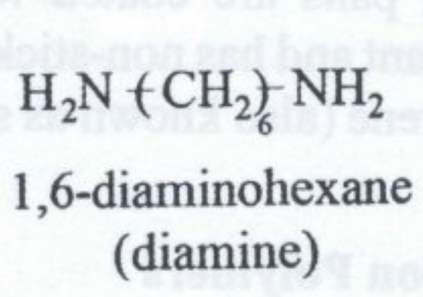
The repeat unit of terylene is  .

(ii) Polyamides

Nylon is an example of polyamides. Nylon is the first synthetic fibre made from a dicarboxylic acid and a diamine. For example, nylon 6,6 is formed from the reaction of an acid monomer (adipic acid) and an amine monomer (1,6-diaminohexane).

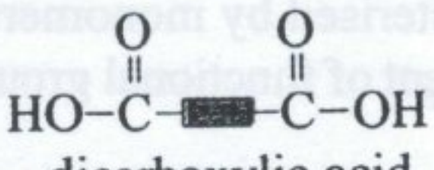


adipic acid
(dicarboxylic acid)

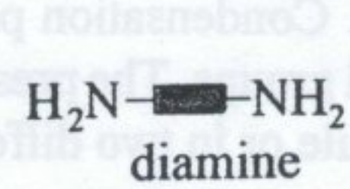


1,6-diaminohexane
(diamine)

The two monomers are represented as follows:

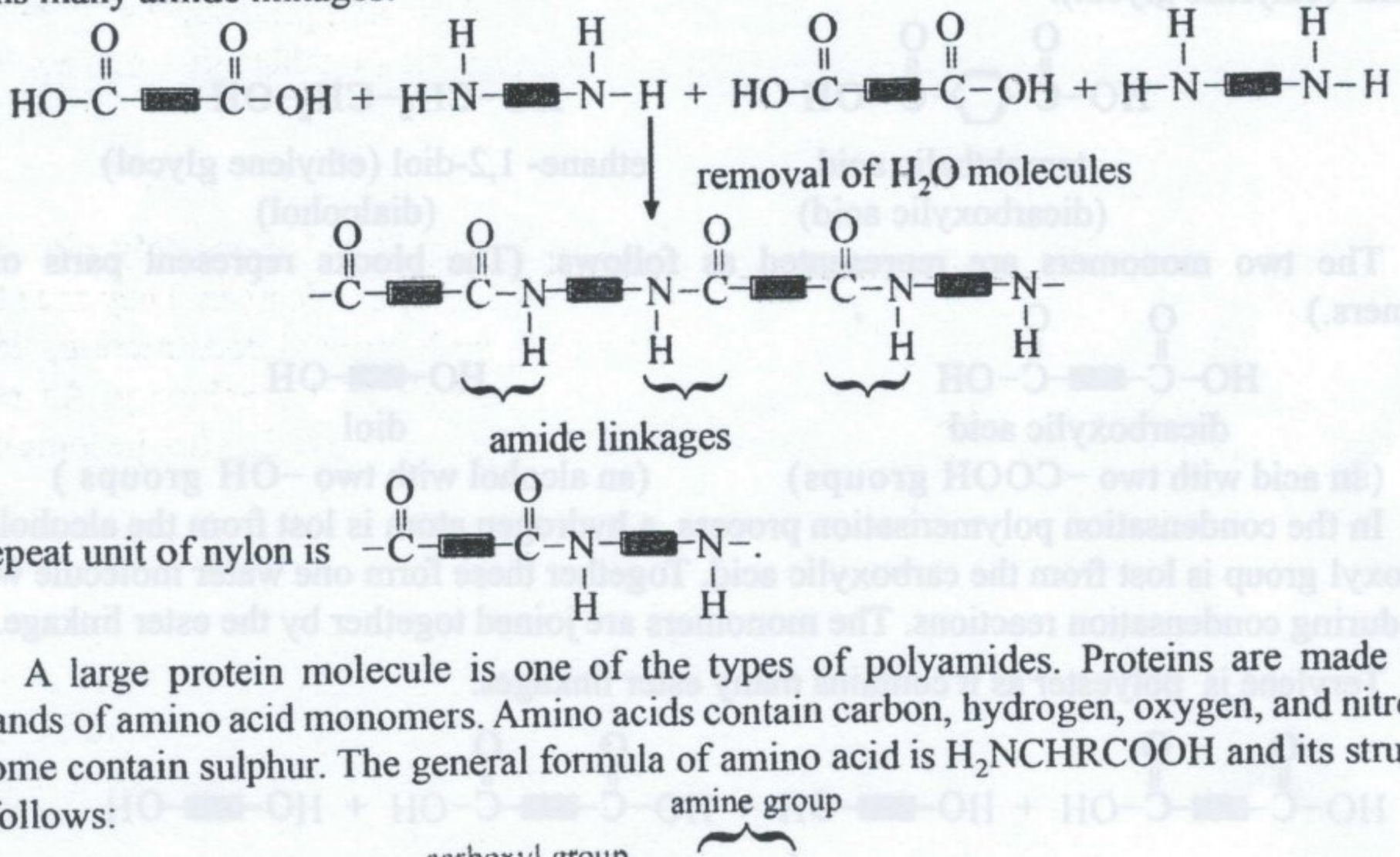


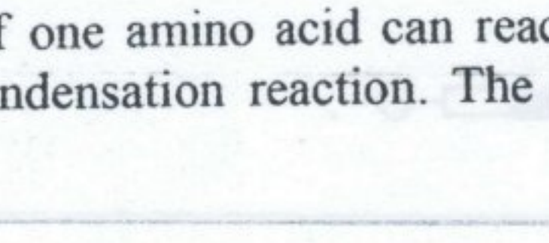
dicarboxylic acid
(an acid with two $-COOH$ groups)



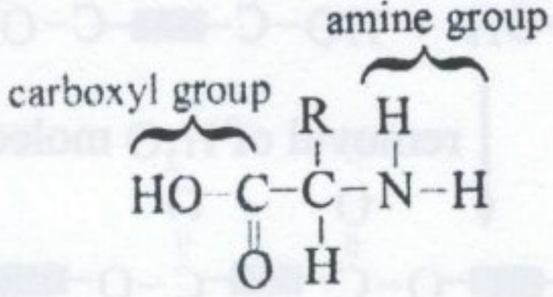
diamine
(an amine with two $-NH_2$ groups)

In the reaction, a water molecule is produced from each pair of monomers. A new bond is formed between nitrogen and carbon atoms to form an amide linkage. Nylon is a polyamide as it contains many amide linkages.



The repeat unit of nylon is  .

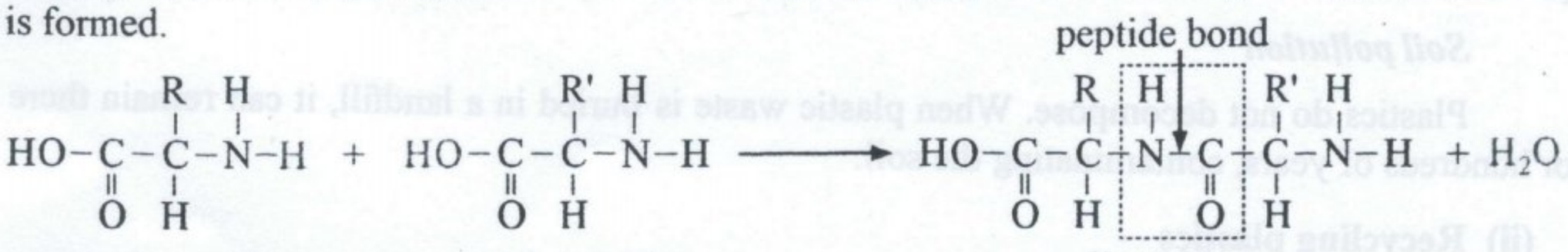
A large protein molecule is one of the types of polyamides. Proteins are made from thousands of amino acid monomers. Amino acids contain carbon, hydrogen, oxygen, and nitrogen, and some contain sulphur. The general formula of amino acid is $H_2NCHRCOOH$ and its structure is as follows:



There are 20 different amino acids commonly found in proteins. Each amino acid differs in terms of its -R group.

The $-NH_2$ group of one amino acid can react with the -COOH of another amino acid to form a dipeptide by a condensation reaction. The covalent bond formed between these two

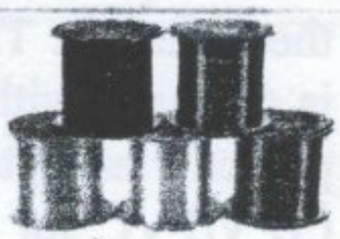
amino acids is called a peptide bond (amide link). Additional amino acids can then react to form a tripeptide, a tetrapeptide, and so on. Eventually, a polypeptide, containing many peptide bonds, is formed.



A polypeptide chain may contain 50 to 2000 amino acids. An amino acid unit within a polypeptide chain is called an amino acid residue.

(iii) Properties and uses

Condensation polymers often have lower molecular masses than addition polymers. The presence of polar functional groups on the chains often enhances chain-chain attractions, particularly if hydrogen bonding is involved, and thus, crystallinity and tensile strength increase.


Fishing lines

Terylene is resistant to stretching and shrinking. It is easily washed and dry quickly. It is being used more and more in textiles. It is stretched out into fibres and can then be made into fabric and articles of clothing. In the home, polyesters are used to make clothing, carpets, curtains, sheets and pillows. Nylon is very strong and resistant, and is used in fishing line, shoes, toothbrush bristles, guitar strings and machine parts.

(d) Plastics and Environment

Plastics are particular types of polymers that can be moulded. Increasingly, plastics can be used in place of natural materials such as wood, metal, cotton, and leather. They are utilised in practically almost every industry, including packaging, building and construction, textiles, consumer goods, transportation, electronic equipment, and industrial machinery. As rapidly increasing production and use of disposable plastic products, plastic pollution has become one of the most pressing environmental issues.

(i) Plastics and pollution

Since plastics are relatively cheap, easily moulded into various shapes, light, tough, waterproof and are resistant to decay, rusting and chemical attack, they are always in demand than other materials for numerous applications. However, plastics are non-biodegradable, that is, they cannot be broken down by bacteria in the soil. So they can take hundreds of years to decompose and throwing away plastics creates rubbish that will pollute the environment for centuries.

Air pollution

Plastics are mostly flammable. Upon incineration, they produce poisonous gases. For example, PVC produces corrosive hydrogen chloride gas during combustion.

Water pollution

Plastics that are thrown into the sea endanger marine animals. For example, turtles often mistake plastic bags for food and choke on them. Plastics may clog up rivers and drains,

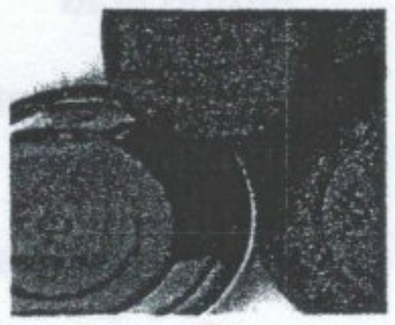
increasing the flooding in the area and serving as a breeding ground for bacteria and germs that spread disease.

Soil pollution

Plastics do not decompose. When plastic waste is buried in a landfill, it can remain there for hundreds of years, contaminating the soil.

(ii) Recycling plastics

The easiest way to deal with plastics is to reuse or recycle them. When plastics are recycled, the various types must be separated from one another. To aid in the separation, manufacturers require to place a recycling symbol on their products to indicate the type of plastic it is.



Recyling symbols

Recycling symbols

These symbols consist of three arrows around one of seven numbers; an abbreviation below the symbol indicates the type of polymer used to make the container. The lower the number in the middle of the symbol, the greater is the ease with which the material can be recycled. (1) PETE/PET stands for polyethylene terephthalate, (2) HDPE for high-density polyethylene, (3) V/PVC for polyvinyl chloride, (4) LDPE for low-density polyethylene, (5) PP for polypropylene, (6) PS for polystyrene, and (7) for all other plastics. These symbols are usually mentioned on plastic products.

(iii) Degradable plastics

Chemists are now developing degradable plastics that break down when they are discarded. The use of degradable plastics is becoming more common as people become increasingly aware of the challenges associated with the disposal of polyalkenes due to their non-biodegradability caused by their lack of reactivity. Developments of biodegradable plastics and photodegradable plastics are able to solve the problem of plastics.

Biodegradable plastics

Some plastics, when buried for many years, eventually become brittle and break down into smaller pieces that can be decomposed naturally by microorganisms in the soil. The smaller pieces of plastics have larger surface areas, and hence, it could degrade much more quickly when it is buried in soil. To degrade plastics naturally by microorganisms (bacteria and fungi), plastics should contain small amounts of starch granules.

Biodegradable plastics are made from monomers derived directly from plant materials, such as polylactic acid (PLA). For instance, PLA which is made from fermented plant starch (usually corn), is now being used as a biodegradable alternative to petroleum-based plastics.

Photodegradable plastics

Polymer chains also have been designed that incorporate carbonyl groups (C=O) at intervals down their length. These carbonyl groups absorb energy from the ultraviolet rays of sunlight to weaken and break down. As the polymer breaks into smaller fragments, the plastic will biodegrade much more quickly.

REVIEW QUESTIONS

(1) CH_2=CHCl monomer is a reactant in a polymerisation reaction.
   (a) Give the structural formula of the polymer that is formed in this polymerisation reaction.
   (b) Is the reaction an addition or a condensation reaction?
(2) (a) Draw the structure of terylene showing two repeat units.
   (b) Name the linkage in terylene.
(3) Name and give the formulae of the two functional groups present in all amino acids.

Key Terms

- **Polymer** is a large molecule made by linking together repeating units of small molecules.
- **Monomer** is a small, reactive molecule that reacts to make long-chain molecules called polymers.
- **Homopolymer** is a polymer that contains only one kind of monomer.
- **Copolymer** is a polymer formed from two or more different monomers.
- **Polymerisation** is the process of linking up monomers to form a polymer.
- **Addition polymerisation** is the polymerisation in which monomers containing carbon-to-carbon double bonds react together to form long-chain molecules.
- **Condensation polymerisation** is a polymerisation in which two molecules are joined to form a larger molecule by elimination of a small molecule, such as H_2O.
- **Biodegradable plastics** are plastics that are designed to break up when exposed to the presence of microorganisms.
- **Photodegradable plastics** are plastics that are gradually broken down with exposure to light.

Chemistry in Society

- When an ant bites, it injects the acidic liquid (formic acid) into the skin.
- Rancid butter has a foul smell because of the presence of butanoic acid.
- Most esters have the fragrant smell of fruits. For example, methyl butanoate smells like an apple and ethyl butanoate smells like a pine apple.
- No-touch or non-contact infrared thermometers measure temperature through the forehead from a close distance in seconds.

- Hair contains a special class of proteins called keratins, which are also present in wool, nails, hoofs, and horns.
- Silk, a macromolecule, comes from the cocoon of the silkworm.
- The windscreen of cars are made of perspex, a solid transparent plastic made of polymethyl methacrylate.
- In the biomedical field, biodegradable polymers find immense use in drug delivery and tissue engineering.

EXERCISES

Q 1 to Q 5 (Understanding)

1. State TRUE or FALSE for each of the following. If FALSE, correct it.
   (a) The dehydrogenation of secondary alcohols gives ketones.
   (b) An ester has a higher boiling point than its corresponding carboxylic acid.
   (c) The greater the polarity of the bond, the stronger its IR absorption.
   (d) An amino acid is a protein monomer.
   (e) Polyethene is a plastic that can be decomposed by microorganisms.

2. Fill in the blanks with a suitable word or phrase or symbol as necessary.
   (a) Heating a mixture of ethanol and ethanoic acid in the presence of concentrated H_2SO_4 produce a fruity smelling compound. This reaction is called _____ .
   (b) The presence of a _____ group in an aldehyde or ketone can be easily tested with 2,4–dinitrophenylhydrazine.
   (c) $H_2C{=}CH_2$ is the monomer of _____ .
   (d) Nylon is the polymer obtained by _____ polymerisation reaction.
   (e) Polypeptides are formed when several _____ are linked together.

3. Choose the correct term or terms given in the brackets.
   (a) Butanal contains (carboxyl, carbonyl, hydroxyl) functional group.
   (b) An ester ($HCOOCH_3$, $HCOOC_2H_5$, CH_3COOCH_3) is produced by the reaction between methanol and methanoic acid.
   (c) If a molecule has a broad band at 3200 cm^{-1} and a sharp band at 1711 cm^{-1} in the IR spectrum, the molecule is most likely an (ester, alcohol, carboxylic acid).
   (d) Condensation polymerisation cannot be formed by using the repeating unit of a monomer (Cl –C6H4– Cl, HO –C6H4– OH, HOOC –C6H4– COOH).
   (e) Nylon is a (polyamide, polyester, polyethene).

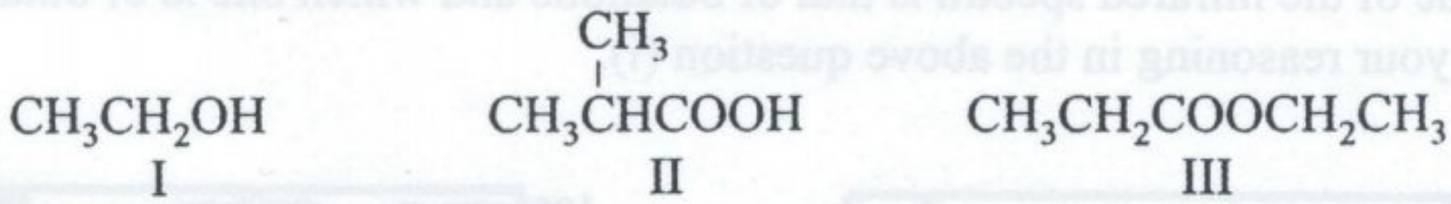
4. Match each of the items given in **List A** with the appropriate item in **List B**.

List A	List B
(a) polylactic acid	(i) IR vibrational mode
(b) diethyl ether	(ii) build-up of amino acids
(c) terylene	(iii) an anaesthetic agent
(d) stretching	(iv) biodegradable plastic
(e) proteins	(v) synthetic polyester

5. Give one word for each of the following descriptions:
   (a) The common name of dimethyl ketone
   (b) The instrument used to obtain an infrared spectrum
   (c) A chain of monomers joined by covalent bonds
   (d) A polymerisation reaction that produces a water molecule for every two monomers that bond
   (e) The linkage that forms between an alcohol and a carboxylic acid monomer during a polymerisation reaction
   (f) The bond that connects amino acids in a protein

Q 6 to Q 19 (Critical Thinking)

6. Refer to the numbered compounds below, answer the questions that follow:

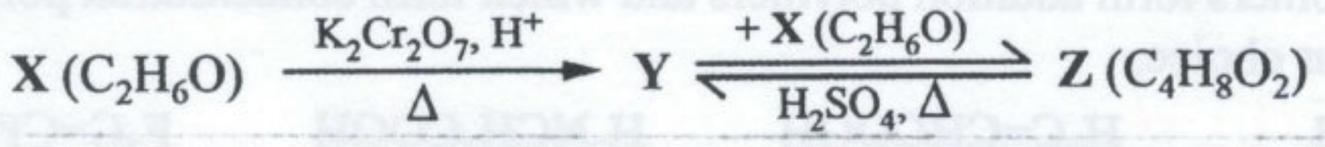


CH_3CH_2OH (I) $CH_3CH(CH_3)COOH$ (II) $CH_3CH_2COOCH_2CH_3$ (III)

(i) Which one of the above compounds is produced from the fermentation of starch or sugar?
(ii) Which classes do the above organic compounds belong to?
(iii) What are the IUPAC names for compounds II and III?

7. Write a balanced chemical equation for the following reactions:
(a) the complete combustion of butanoic acid
(b) the reduction of butanoic acid

8. Compound **X** (C_2H_6O) is an alcohol. On oxidation, **X** produces **Y**. **Y** reacts again with **X** to form **Z** ($C_4H_8O_2$). **Z** is a sweet smelling liquid. Identify **X**,**Y** and **Z**.



$$\mathbf{X}\,(C_2H_6O) \xrightarrow[\Delta]{K_2Cr_2O_7,\ H^+} \mathbf{Y} \underset{H_2SO_4,\ \Delta}{\overset{+\,\mathbf{X}\,(C_2H_6O)}{\rightleftharpoons}} \mathbf{Z}\,(C_4H_8O_2)$$

9. A mixture of ethanoic acid and methanol is warmed in the presence of concentrated sulphuric acid.
(i) Using structural formulae, give a balanced equation for the reaction which takes place.
(ii) What is the IUPAC name of the organic compound formed in this reaction?

10. (a) What carboxylic acids and alcohols would you use to make the following esters?
(i) butyl methanoate (ii) ethyl methanoate (iii) propyl propanoate
(b) What esters would be made using the following carboxylic acids and alcohols?
(i) ethanoic acid and *n*-butanol (ii) propanoic acid and ethanol
(c) Draw the structures of the following esters:
(i) ethyl methanoate (ii) propyl ethanoate
(d) Give two uses of esters.

11. Qualitative chemical tests are carried out on the organic compound. The results are shown below.

Test	2,4-DNP	Fehling's reagent
Observation	Orange precipitate	No observable change

Determine the type of organic compound. Explain your reasoning. (No chemical equation is required.)

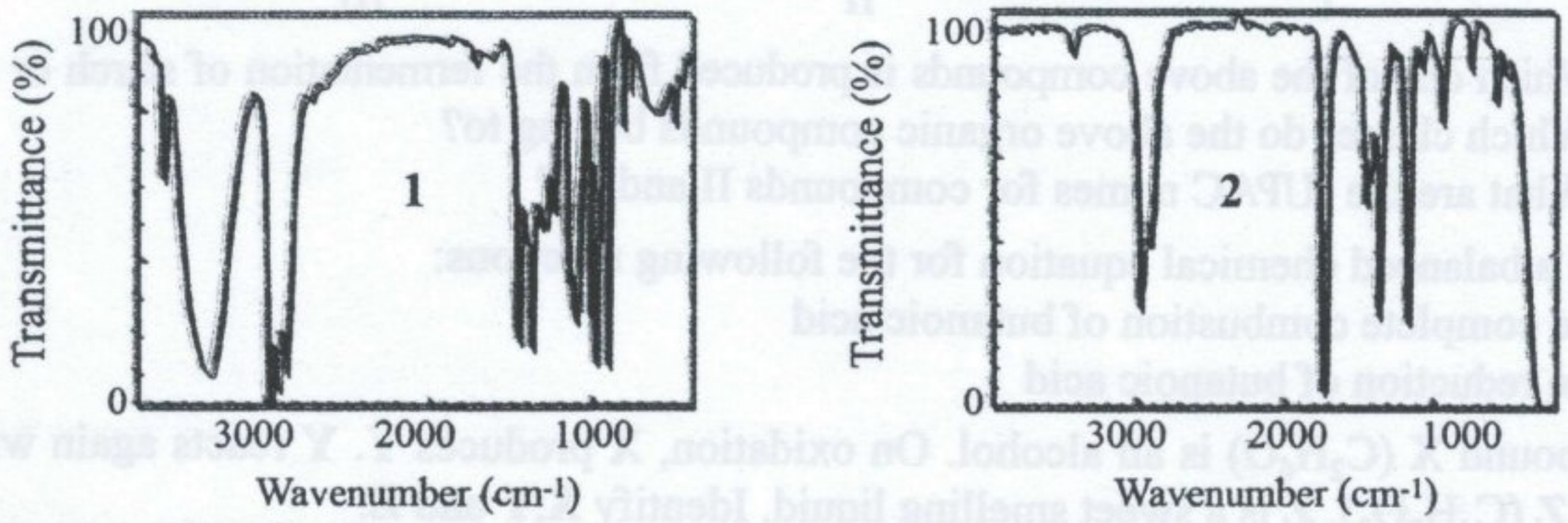
12. Identify each of the following compounds as either a carboxylic acid, ester, amine or aldehyde.

$CH_3CH_2CH_2COOH$, $H_2NCH_2CH_3$, $CH_3COOCH_2CH_2CH_3$, CH_3CHO

(i) Give the IUPAC name of each compound.
(ii) How can you identify an aldehyde compound by a simple chemical test?

13. How could IR spectroscopy distinguish between $CH_3CH_2CH_2OH$ and $CH_3CH_2OCH_3$?

14. Look at the two infrared spectra below.
(i) Which one of the infrared spectra is that of butanone and which one is of butanol?
(ii) Explain your reasoning in the above question (i).



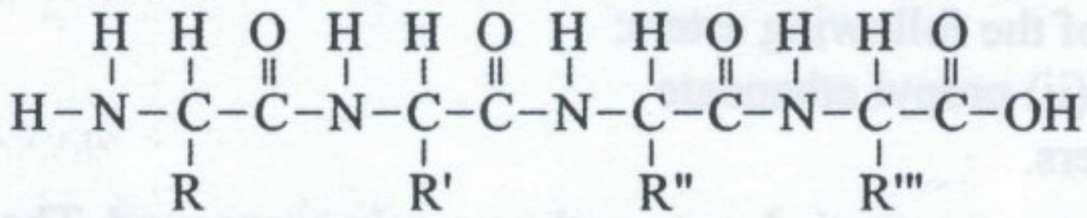
15 (a) Which of these monomers form addition polymers and which form condensation polymers? Give reasons for your choice.

$H_2NCH(CH_3)COOH$ $H_2C{=}CHCOOH$ H_2NCH_2COOH $F_2C{=}CF_2$

(b) Write a chemical equation to show the polymerisation reaction between propene molecules. What is the repeat unit of polypropene?

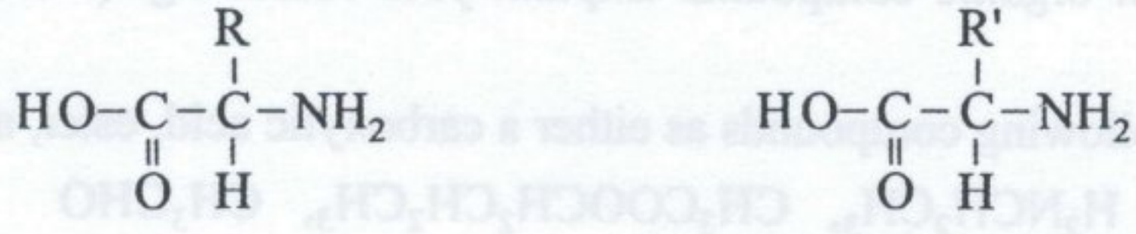
16. An amino acid has the formula $H_2NCH(CH_2CH_2SCH_3)\,COOH$.
(a) Give the structural formula of this amino acid .
(b) What is the chemical formula of the polymer that is produced?
(c) Are there any peptide bonds in this polymer? Give a reason for your answer.

17. The following polypeptide is the end product of a polymerisation reaction:



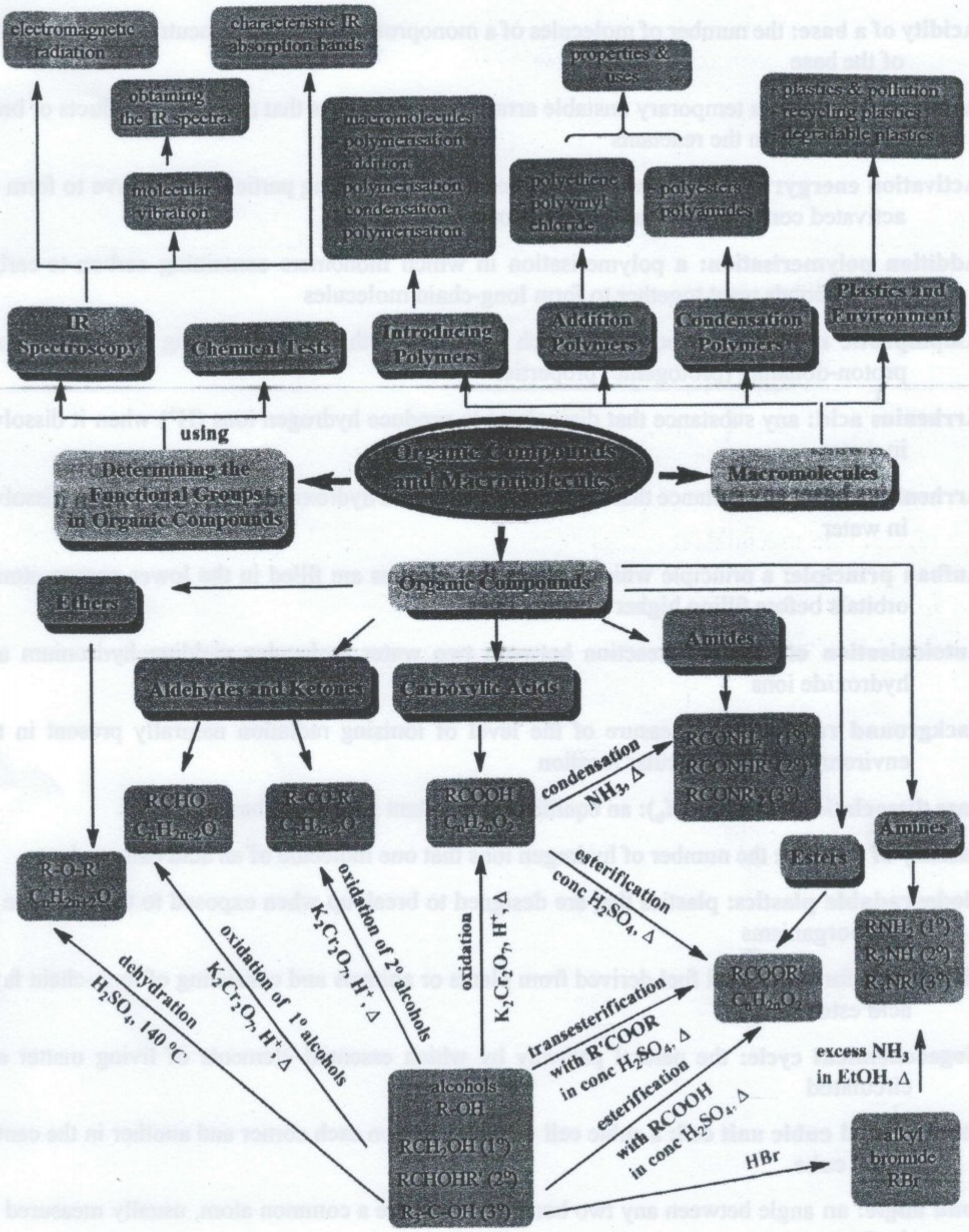
(a) Give the structural formulae of the monomers that make up the polypeptide.
(b) Label the amine group and the carboxyl group of one monomer.
(c) Name the bond that forms between the monomers of the polypeptide.

18. Give the structural formula for a polypeptide chain, consisting of two molecules of amino acid **A** and one molecule of amino acid **B**.



19. Explain the term photodegradable. Clarify how the production of photodegradable polymers is designed to break down.

CHAPTER REVIEW
(Concept Map)



GLOSSARY

Acid dissociation constant (K_a): an equilibrium constant for a weak acid

Acidity of a base: the number of molecules of a monoprotic acid that will neutralise one molecule of the base

Activated complex: a temporary unstable arrangement of atoms that may form products or break apart to reform the reactants

Activation energy: the minimum amount of energy that reacting particles must have to form the activated complex and lead to a reaction

Addition polymerisation: a polymerisation in which monomers containing carbon-to-carbon double bonds react together to form long-chain molecules

Amphiprotic molecule: a molecule which can have both proton-accepting (protophilic) and proton-donating (protogenic) properties

Arrhenius acid: any substance that dissociates to produce hydrogen ions (H^+) when it dissolves in water

Arrhenius base: any substance that dissociates to produce hydroxide ions (OH^-) when it dissolves in water

Aufbau principle: a principle which states that electrons are filled in the lower energy atomic orbitals before filling higher energy ones

Autoionisation of water: a reaction between two water molecules yielding hydronium and hydroxide ions

Background radiation: a measure of the level of ionising radiation naturally present in the environment at a particular location

Base dissociation constant (K_b): an equilibrium constant for a weak base

Basicity of an acid: the number of hydrogen ions that one molecule of an acid can produce

Biodegradable plastics: plastics that are designed to break up when exposed to the presence of microorganisms

Biodiesel: a form of diesel fuel derived from plants or animals and consisting of long-chain fatty acid esters

Biogeochemical cycle: the natural pathway by which essential elements of living matter are circulated

Body-centred cubic unit cell: a cubic cell with an atom on each corner and another in the centre of the cube

Bond angle: an angle between any two bonds that include a common atom, usually measured in degrees

Bond energy (Bond enthalpy): amount of energy required in bond breaking or making of one mole of chemical bonds in a molecular element or compound

Bonding pair: pair of electrons being shared between two atoms in a molecule

Brønsted-Lowry acid: any substance that can donate a proton

Brønsted-Lowry base: any substance that can accept a proton

Buffer solution: solution that resists changes in pH as a result of dilution or a small addition of acids or bases

Catalyst: substance that alters the rate of a chemical reaction but remains chemically unchanged at the end of the reaction

Closed system: a system that allows energy to enter and exit, but matter can neither be gained nor lost

Collision theory: a theory which states that a chemical reaction only takes place when two reacting molecules collide in the correct orientation with sufficient kinetic energy

Complex ion: an ion which has a metal ion at its centre with a number of other molecules or ions surrounding it

Condensation polymerisation: a polymerisation in which two molecules are joined to form a larger molecule by elimination of a small molecule, such as H_2O

Condensation reaction: the reaction in which a small molecule, such as water, is eliminated when two molecules are joined

Conjugate acid: a species that forms when a base gains a proton

Conjugate acid-base pair: an acid-base pair that consists of either an acid and its conjugate base or a base and its conjugate acid

Conjugate base: a species that forms when an acid loses a proton

Coordinate bond (Dative bond): a covalent bond that consists of a pair of electrons donated by only one of the two bonded atoms

Coordination number: the number of atoms or molecules or ions surrounding a central atom in a complex

Copolymer: a polymer formed from two or more different monomers

Crystal lattice: a geometric arrangement of the points in space at which the atoms, molecules, or ions of a substance occur

Diamagnetic substance: a substance that has no unpaired electrons and shows no attraction (slight repulsion) from the external magnetic field

Dipole moment: a measure of the polarity of a covalent bond

Dipole: a pair of charges that are equal in magnitude and opposite in charge that is separated by a distance

Dipole-dipole interaction: an interaction that results when two dipolar molecules interact with each other

Dynamic equilibrium: an equilibrium in which the chemical reaction is still proceeding at equal rates of the forward and reverse reactions, and the concentrations of the reactants and products remain constant

Electromagnetic radiation: the radiant energy that displays wave properties

Electron-deficient molecule: a molecule in which there is an insufficient number of valence electrons to complete the octet of the central atom

Electrostatic attraction: the attraction between a negatively charged ion and a positively charged ion

Endothermic reaction: a reaction which absorbs heat from the surroundings

Energy transformation: the process of changing one form of energy into another

Enthalpy change: the heat change accompanying a chemical reaction at constant pressure

Enzymes: proteins that act as catalysts for specific biochemical reactions

Equilibrium constant: a ratio that expresses the relationship between the amounts of products and reactants present at equilibrium in a reversible chemical reaction at a given temperature

Esterification: the reaction of an alchol with an acid to produce an ester and water

Exothermic reaction: a reaction which releases heat into the surroundings

Expanded valence shell molecule: a molecule in which there are more than 8 electrons in the valence shell of the central atom

Face-centred cubic unit cell: a cubic cell with an atom on each corner, and an atom at the centre of each face

Ferromagnetic substance: a substance that is strongly attracted by the applied magnetic field, and retains its magnetisation for some time even after the external magnetic field is removed

Fissile heavy atoms: materials capable of sustaining a nuclear fission chain reaction

Frequency: the number of wave crests that pass by a given point in one second

Giant covalent structure: a three-dimensional structure of atoms that are joined by covalent bonds

Green chemistry: the design of chemical products and processes that reduce or eliminate the generation of hazardous substances

Heterogeneous catalyst: a catalyst which is in a different phase from the reactants in a catalysed reaction

Heterogeneous equilibrium: a chemical equilibrium in which the reactants and the products are all in more than one phase

Homogeneous catalyst: a catalyst which is in the same phase as the reactants in a catalysed reaction

Homogeneous equilibrium: a chemical equilibrium in which the reactants and the products are all in a single phase

Homopolymer: a polymer that contains only one kind of monomer

Hund's rule: every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

Hydrogen bonding: the electrostatic attraction between a hydrogen atom in one polar molecule and a small electronegative atom (as of oxygen, nitrogen, or fluorine) in another molecule of the same or different polar substances

Infrared spectroscopy: a technique for identifying compounds based on the change in vibrations of particular atoms when infrared radiation of specific frequencies is absorbed

Intermolecular forces: the weak forces between atoms, molecules, and ions

Intermolecular hydrogen bonds: the hydrogen bonds that occur between two atoms of same or different molecules

Ion-dipole interaction: an interaction that results from the electrostatic interaction between an ion and a neutral molecule that has a dipole

Ionic compounds: compounds that consist of ions and predominantly contain ionic bonding

Ionic product of water: the equilibrium constant for the autoionisation of water which is the product of the molar concentrations of H^+ and OH^- ions at a particular temperature

Law of Conservation of Energy: in any physical or chemical process, energy can neither be created nor destroyed

Lewis acid: any substance that can accept an electron pair

Lewis base: any substance that can donate an electron pair

London dispersion force: a temporary attractive force that results from the temporary dipoles formed due to the occupying positions of electrons in two adjacent atoms

Lone pair (unshared pair): pair of electrons that is not involved in bonding with other atoms

Molecular orbital (MO) theory: a method for describing the electronic structure of molecules based on quantized energy levels

Molecular shape: the three-dimensional arrangement of the atoms that constitute a molecule

Monomer: a small, reactive molecule that reacts to make long-chain molecules called polymers

Negative catalyst: a catalyst that decreases the rate of a chemical reaction

Neutral aqueous solution: a solution in which the concentrations of hydrogen ions and hydroxide ions are equal at the value of 1.0×10^{-7} mol dm^{-3} at 25 °C (298 K) (pH = 7)

Non-polar covalent bond: a covalent bond in which the bonding electrons are shared equally between two atoms

Non-polar molecules: molecules that have an equal distribution of charge

Ocean acidification: a reduction in the pH of the ocean over an extended period of time, caused primarily by the uptake of carbon dioxide from the atmosphere

Organisms: living biological entities, such as animals, plants, fungi, or bacteria

Paramagnetic substance: a substance that has unpaired electrons and shows weak attraction towards the external magnetic field

Pauli's exclusion principle: no more than two electrons can occupy the same orbital, and two electrons in the same orbital must have opposite spins

Persistent organic pollutants (POPs): carbon-based organic compounds that have the special abilities to be long-lasting and to resist breakdown into safer substances

pH: the negative logarithm to base 10 of the molar concentration of the hydrogen ions

Phase: a portion of a physical state (solid, liquid, gas) that is homogeneous throughout, and can be separated physically from other phases

Phosphorus cycle: a biogeochemical cycle that describes the movement of phosphorus through the lithosphere, hydrosphere, and biosphere

Photochemical reaction: a chemical reaction initiated by the absorption of light energy

Photodegradable plastics: plastics that are gradually broken down with exposure to light

Photodegradation: a process by which substances are broken down by the action of sunlight

pOH: the negative logarithm to base 10 of the molar concentration of the hydroxide ions

Polar covalent bond: a covalent bond in which the bonding electrons is unequally shared between two atoms

Polar molecule: a molecule in which one end of the molecule is slightly positive while the other end is slightly negative

Polarity: a separation of charge, leading to one part of a bond or molecule becoming positively charged and the other negatively charged

Polymer: a large molecule made by linking together repeating units of small molecules

Polymerisation: the process of linking up monomers to form a polymer

Positive catalyst: a catalyst that increases the rate of a chemical reaction

Primary alcohol: an alcohol with a $-CH_3$ or $R-CH_2-$ group bonded to the -OH group

Radioactivity: the process by which the nucleus of an unstable atom loses energy by emitting radiation, including alpha particles, beta particles, and gamma rays

Rate of a reaction: the change in amount of a reactant or a product per unit of time

Reversible reaction: a reaction that can proceed in the forward as well as in the reverse directions under the appropriate conditions

Salt hydrolysis: the reaction of an anion or a cation of salt, or both, with water

Secondary alcohol: an alcohol with two R- groups bonded to the carbon bearing the -OH group

Simple cubic unit cell: a cubic cell with an atom in each corner of the cube

Specific heat capacity of liquid: the energy required to raise the temperature of 1 g of liquid by 1 °C

Spectroscopy: the study of the interaction of matter and electromagnetic radiation

Strong acids: acids (strong electrolytes) that completely ionise in water

Strong bases: bases (strong electrolytes) that ionise completely in water

Successful collision: a collision that causes a chemical reaction

Sulphur cycle: a biogeochemical cycle in which the sulphur moves between rocks, waterways, atmosphere, and living systems

Surroundings: everything in the universe other than the system

System: the specific part of the universe that contains the reaction or process which is studied

Transesterification: the reaction of an ester with an alcohol to form a different ester

Transition elements: the elements that have partially filled *d* subshells (orbitals) which can give rise to cations with incomplete *d* subshells (orbitals)

Transition state (an intermediate state): a highly energetic state that would be highly unstable

Unit cell: the smallest repeating unit of a crystal lattice that shows the three-dimensional pattern of the entire crystal

Valence electrons: the electrons in the outermost shell of an atom

Valence Shell Electron Pair Repulsion (VSEPR) theory: to predict the shapes of molecules and ions, based on the repulsive interactions of the electrons around a central atom

van der Waals forces: weak intermolecular forces that bind molecules together

Volatile organic compounds (VOCs): organic chemicals that can vaporise

Wavelength: the distance from any point on one wave to the corresponding point on the next wave

Wavenumber: the number of wave crests that pass in one centimetre

Weak acids: acids (weak electrolytes) that partially ionise only to a limited extent in water

Weak bases: bases (weak electrolytes) that ionise to a very limited extent in water

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THE GOVERNMENT OF
THE REPUBLIC OF THE UNION OF MYANMAR

MINISTRY OF EDUCATION

TEXTBOOK

CHEMISTRY

GRADE 12

နိုင်ငံတော်က အခမဲ့ထောက်ပံ့ပေးသည်။

BASIC EDUCATION CURRICULUM AND TEXTBOOK COMMITTEE

2023-2024

၂၀၂၃ ခုနှစ်၊ မတ်လ၊ အုပ်ရေ - ၃၆၉၂၁၅

၂၀၂၃-၂၀၂၄ ပညာသင်နှစ်

အမျိုးသားသင်ရိုးညွှန်းတမ်းကော်မတီကအတည်ပြုသည်။

အခြေခံပညာသင်ရိုးညွှန်းတမ်းနှင့် ကျောင်းသုံးစာအုပ်ကော်မတီ၏

မူပိုင်ဖြစ်သည်။

အလုပ်အမိန့်အမှတ် - L ၀၈/၂၃ ဖြင့်
တော်ဝင်မြင့်မိုရ်ကုမ္ပဏီ ပုံနှိပ်တိုက် ရန်ကုန်မြို့တွင် ပုံနှိပ်သည်။

PREFACE

Chemistry is an area of knowledge remarkable for its breadth and depth. Some understanding of chemistry will help deal with major social issues that lie ahead in the 21st century. Nowadays, people are facing environmental issues, due to the results of the harmful effects of technology. By studying chemistry, one should understand why the harmful effects occurred and how the risk can be reduced for future generations. This textbook will give students the basics of chemistry along with some perception of the role of chemistry in both positive and negative aspects of the world today. Learning about the benefits and risks associated with our chemicals will help students to be informed citizens, and able to make intelligent choices concerning the world around them.

Additionally, studying chemistry teaches the student to solve problems and communicate with others in an organised and logical manner. By participating actively in all lessons, they will achieve soft skills/employability skills, including the **5 Cs** which will be helpful in their further study and throughout their career.

21st Century Skills

After learning this course, students will enable to participate actively in all lessons through the **5 Cs** as important **21st century skills for learning:**

- ✓ **Collaboration** – In lessons, students will be working in groups, to share ideas with their classmates and find the solution together.
- ✓ **Communication** – Students will develop verbal and non-verbal communication skills in group work.
- ✓ **Critical thinking and problem solving** – Students will be given interesting problems to solve – finding and explaining solutions, and looking for correcting errors.
- ✓ **Creativity and innovation** – Thinking 'outside the box' is an important 21st century skill. Students will be encouraged to explore new ideas and solve problems in new ways.
- ✓ **Citizenship** – Students will take part in the school community and develop fairness and conflict resolution skills.

Important Features of This Textbook

- ✦ The High School Chemistry Curriculum covers **six main themes**: Particulate Nature of Substances, Periodicity, Chemical Calculations, Chemistry of Reactions, The Environment, and Organic Chemistry.
- ✦ The Grade 12 Chemistry Textbook consists of **eight chapters**.
  - Chapter 1: Chemical Bonding and Intermolecular Forces
  - Chapter 2: Energy Changes in Chemical Reactions
  - Chapter 3: Chemical Kinetics: Rates of Reaction
  - Chapter 4: Chemical Equilibrium
  - Chapter 5: Acid-Base Reactions
  - Chapter 6: Transition Elements
  - Chapter 7: Chemistry and Green Environment
  - Chapter 8: Organic Compounds and Macromolecules

- Each chapter starts with the ***introduction*** of the topic, containing an example of how the material is covered in the chapter, followed by the **Learning Outcomes** of the chapter.
- Each section of the chapter also starts with a brief introduction, followed by sub-sections. The text and illustrations describe and explain all of the facts and concepts that students need to know. Worked examples show students how to solve the problem before they are asked to tackle problems on their own. **Review Questions** after each section, and give students a chance to check that they have understood the topic they have just read about. It will be noted that the more important terms are set off in bold type when first introduced. Thorough definitions of these terms are presented at the end of each section under **Key Terms**. These terms are also defined in the Glossary which is provided to help students review key terms, at the end of the Textbook.
- The end-of-chapter **Exercises** provide practice and review of the chapter material, to ensure that students have grasped major concepts, in addition to testing their understanding of the materials covered in the chapter. At the end of each chapter, the **Chapter Review** (a concept link) guides students in determining the most important concepts in the chapter as well as the highlights of the chapter.
- In addition, the "**Chemistry in Society**" highlighted in colour, introduces students to the important chemicals and substances that are the basis for the high standard of living and modern technology as well as that chemistry is intimately involved in almost every aspect of our material world. *It is suggested that teachers should not emphasise this section as exam-oriented teaching.*

Goals of Grade 12 Chemistry Textbook

Six fundamental higher-order thinking skills, such as solving skills, inquiring skills, reasoning skills, communicating skills, conceptualising skills, and creative and innovative skills, have been identified in the Chemistry Syllabus.

Knowing something about chemistry adds a new dimension to everyday life. In this chemistry course, students will develop the basic knowledge and skills which will help them to understand more about chemistry and to apply it in their daily life. They will learn how to demonstrate an interest in the creativity and innovation found in chemistry. In some lessons, students will participate in group activities to develop skills in scientific methods of investigation.

They will also recognise the high school chemistry courses as a foundation for vocational applications and further study in science and technology. We hope that students will understand the benefits and hazards of the Material World through the knowledge they learned.

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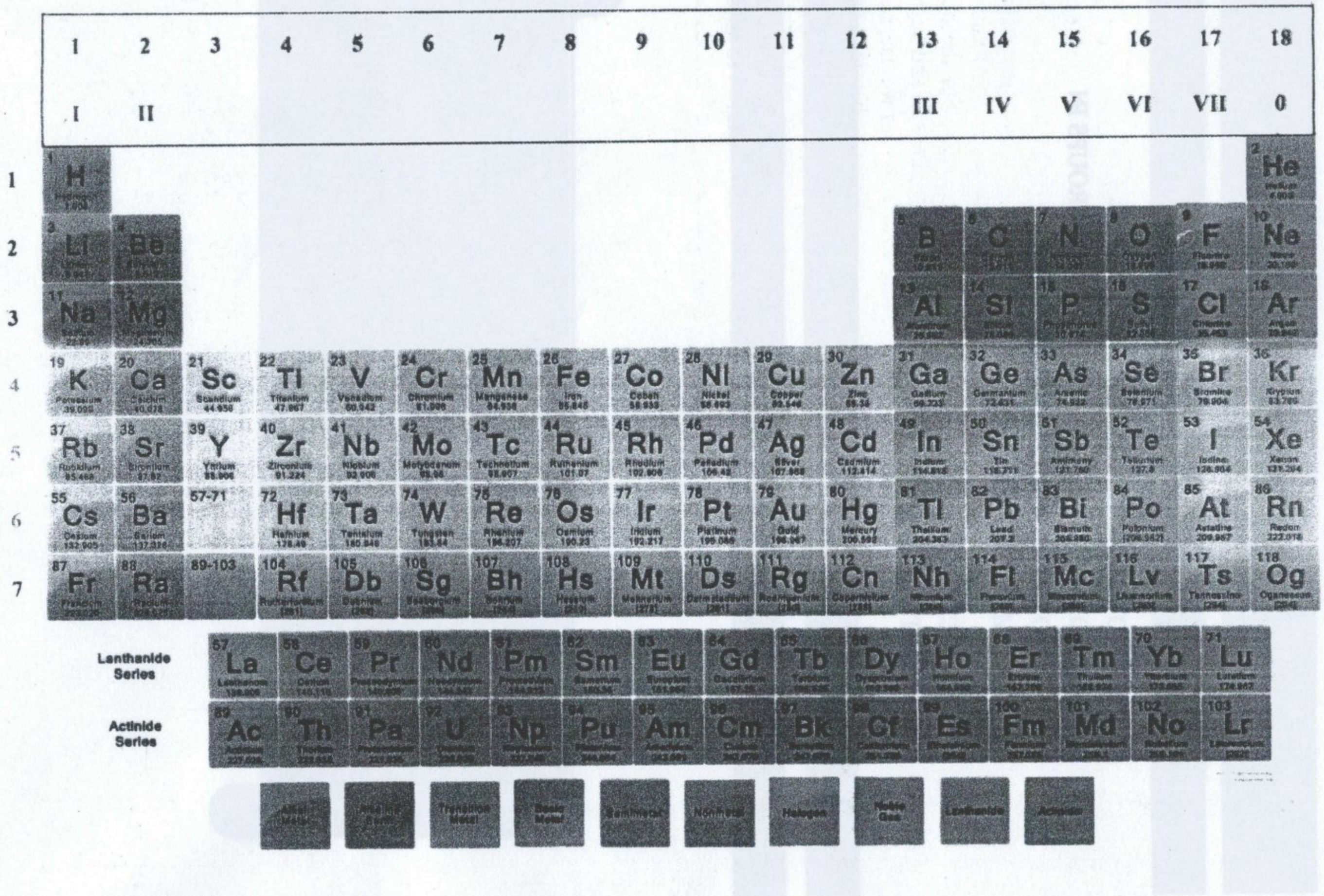
COVER STORY

The six themes - *Chemical Calculations, Periodicity, Particulate Nature of Substances, Chemistry of Reaction, Environment, and Organic Chemistry,* of the Basic Education High School Chemistry Curriculum through the higher order thinking skills, including the 5 Cs as 21st century skills for learning skills are considered important in chemistry education.

The Periodic Table